

Chapter 1. Review of Thermodynamics

This chapter starts with a brief discussion of the subject of statistical physics and thermodynamics, and the relation between these two disciplines. Then I proceed to review the basic notions and relations of thermodynamics. Most of this material is supposed to be known to the reader from their undergraduate studies,¹ so the discussion is rather brief.

1.1. Introduction: Statistical physics and thermodynamics

Statistical physics (alternatively called “statistical mechanics”) and *thermodynamics* are two different but related approaches to the same goal: an approximate description of the “internal”² properties of large physical systems, notably those consisting of $N \gg 1$ identical particles – or other components. The traditional example of such a system is a human-scale portion of gas, with the number N of atoms/molecules³ of the order of the Avogadro number $N_A \sim 10^{24}$ (see Sec. 4 below).

The motivation for the statistical approach to such systems is straightforward: even if the laws governing the dynamics of each particle and their interactions were exactly known, and we had infinite computing resources at our disposal, calculating the exact evolution of the system in time would be impossible, at least because it is completely impracticable to measure the exact initial state of each component – in the classical case, the initial position and velocity of each particle. The situation is further exacerbated by the phenomena of chaos and turbulence,⁴ and the quantum-mechanical uncertainty, which do not allow the exact calculation of positions and velocities of the component particles even if their initial state is known with the best possible precision. As a result, in most situations, only statistical predictions about the behavior of such systems may be made, with *probability theory* becoming a major tool of the mathematical arsenal.

However, the statistical approach is not as bad as it may look. Indeed, it is almost self-evident that any measurable *macroscopic* variable characterizing a stationary system of $N \gg 1$ particles as a whole (think, e.g., about the stationary pressure P of the gas contained in a fixed volume V) is nearly constant in time. Indeed, as we will see below, besides certain exotic exceptions, the relative magnitude of fluctuations – either in time, or among many macroscopically similar systems – of such a variable is of the order of $1/N^{1/2}$, and for $N \sim N_A$ is extremely small. As a result, the *average values* of appropriate macroscopic variables may characterize the state of the system quite well – satisfactory for nearly all practical purposes. The calculation of relations between such average values is the only task of thermodynamics and the main task of statistical physics. (Fluctuations may be important, but due to their smallness, in most cases their analysis may be based on perturbative approaches – see Chapter 5.)

¹ For remedial reading, I can recommend, for example (in the alphabetical order): C. Kittel and H. Kroemer, *Thermal Physics*, 2nd ed., W. H. Freeman (1980); F. Reif, *Fundamentals of Statistical and Thermal Physics*, Waveland (2008); D. V. Schroeder, *Introduction to Thermal Physics*, Addison Wesley (1999).

² Here “internal” is an (admittedly loose) term meaning all the physics unrelated to the motion of the system as a whole. The most important example of internal dynamics is the thermal motion of atoms and molecules.

³ This is perhaps my best chance to reverently mention Democritus (circa 460-370 BC) – the Ancient Greek genius who was apparently the first one to conjecture the atomic structure of matter.

⁴ See, e.g., CM Chapters 8 and 9.

Now let us have a fast look at typical macroscopic variables that statistical physics and thermodynamics should operate with. Since I have already mentioned pressure P and volume V , let us start with this famous pair of variables. First of all, note that volume is an *extensive variable*, i.e. a variable whose value for a system consisting of several non-interacting parts is the sum of those of its parts. On the other hand, pressure is an example of an *intensive variable* whose value is the same for different parts of a system – if they are in equilibrium. To understand why P and V form a natural pair of variables, let us consider the classical playground of thermodynamics: a portion of a gas contained in a cylinder closed with a movable piston of area A (Fig. 1).

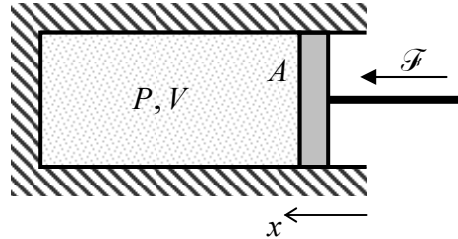


Fig. 1.1. Compressing gas.

Neglecting the friction between the walls and the piston, and assuming that it is being moved so slowly that the pressure P is virtually the same for all parts of the volume at any instant,⁵ the elementary work of the external force $\mathcal{F} = PA$ compressing the gas, at a small piston's displacement $dx = -dV/A$, is

$$d\mathcal{W} = \mathcal{F}dx \equiv -\left(\frac{\mathcal{F}}{A}\right)(-Adx) \equiv -PdV. \quad (1.1) \quad \text{Work on a gas}$$

The last expression is more general than the model shown in Fig. 1, and does not depend on the particular shape of the system's surface. (Note that in the notation of Eq. (1), which will be used throughout this course, the elementary work done *by* the gas *on* its environment equals $-d\mathcal{W}$.)

From the point of analytical mechanics,⁶ V and $(-P)$ are just one of many possible *canonical pairs* of generalized coordinates q_j and generalized forces \mathcal{F}_j , whose products $d\mathcal{W}_j = \mathcal{F}_j dq_j$ give independent contributions to the total work of the environment on the system under analysis. For example, the reader familiar with the basics of electrostatics knows that if the spatial distribution $\mathcal{E}(\mathbf{r})$ of an external electric field does not depend on the electric polarization $\mathcal{P}(\mathbf{r})$ of a dielectric medium placed into this field, its elementary work on the medium is

$$d\mathcal{W} = \int \mathcal{E}(\mathbf{r}) \cdot d\mathcal{P}(\mathbf{r}) d^3r \equiv \int \sum_{j=1}^3 \mathcal{E}_j(\mathbf{r}) d\mathcal{P}_j(\mathbf{r}) d^3r. \quad (1.2a)$$

The most important cases when this condition is fulfilled (and hence Eq. (2a) is valid) are, first, long cylindrical samples in a parallel external field (see, e.g., EM Fig. 3.13) and, second, the polarization of a sample (of any shape) due to that of discrete electric dipoles \mathbf{p}_k , whose electric interaction is negligible. In the latter case, Eq. (2a) may be also rewritten as the sum over the single dipoles located at points \mathbf{r}_k :⁷

⁵ Such slow processes are called *quasistatic*; in the absence of static friction, they are (macroscopically) *reversible*: at their inversion, the system runs back through in the same sequence of its macroscopic states.

⁶ See, e.g., CM Chapters 2 and 10.

⁷ Some of my SBU students needed an effort to reconcile the positive signs in Eq. (2b) with the negative sign in the well-known relation $dU_k = -\mathcal{E}(\mathbf{r}_k) d\mathbf{p}_k$ for the potential energy of a dipole in an external electric field – see, e.g.,

$$d\mathcal{W} = \sum_k d\mathcal{W}_k, \quad \text{with } d\mathcal{W}_k = \mathcal{E}(\mathbf{r}_k) \cdot d\mathbf{p}_k. \quad (1.2b)$$

Very similarly, and at similar conditions on an external magnetic field $\mathcal{H}(\mathbf{r})$, its elementary work on a magnetic medium may be also represented in either of two forms:⁸

$$d\mathcal{W} = \mu_0 \int \mathcal{H}(\mathbf{r}) \cdot d\mathcal{M}(\mathbf{r}) d^3r \equiv \mu_0 \int \sum_{j=1}^3 \mathcal{H}_j(\mathbf{r}) d\mathcal{M}_j(\mathbf{r}) d^3r, \quad (1.3a)$$

$$d\mathcal{W} = \sum_k d\mathcal{W}_k, \quad \text{with } d\mathcal{W}_k = \mu_0 \mathcal{H}(\mathbf{r}_k) \cdot d\mathbf{m}_k. \quad (1.3b)$$

where \mathcal{M} and \mathbf{m}_k are the vectors of, respectively, the medium's magnetization and the magnetic moment of a single dipole. Formulas (2) and (3) show that the roles of generalized coordinates may be played by Cartesian components of the vectors \mathcal{P} (or \mathbf{p}) and \mathcal{M} (or \mathbf{m}), with the components of the electric and magnetic fields playing the roles of the corresponding generalized forces. This list may be extended to other interactions (such as gravitation, surface tension in fluids, etc.). Following tradition, I will use the $\{-P, V\}$ pair in almost all the formulas below, but the reader should remember that they all are valid for any other pair $\{\mathcal{F}_j, q_j\}$.⁹

Again, the specific relations between the variables of each pair listed above may depend on the statistical properties of the system under analysis, but their definitions are not based on statistics. The situation is very different for a very specific pair of variables, *temperature* T and *entropy* S , although these “sister variables” participate in many formulas of thermodynamics exactly as if they were just one more canonical pair $\{\mathcal{F}_j, q_j\}$. However, the very existence of these two notions is due to statistics. Namely, temperature T is an intensive variable that characterizes the degree of thermal “agitation” of the system's components. On the contrary, the entropy S is an extensive variable that in most cases evades immediate perception by human senses; it is a quantitative measure of the *disorder* of the system, i.e. the degree of our ignorance about its exact microscopic state.¹⁰

The reason for the appearance of the $\{T, S\}$ pair of variables in formulas of thermodynamics and statistical mechanics is that the statistical approach to large systems of particles brings some qualitatively new results, most notably the possibility of *irreversible* time evolution of collective (*macroscopic*) variables describing the system. On one hand, irreversibility looks absolutely natural in such phenomena as the diffusion of an ink drop in a glass of water. In the beginning, the ink molecules are located in a certain small part of the system's volume, i.e. are to some extent ordered, while at the late stages of diffusion, the position of each molecule in the glass is essentially random. However, on

EM Eqs. (3.15). The resolution of this paradox is simple: each term of Eq. (2b) describes the work $d\mathcal{W}_k$ of the electric field on the *internal* degrees of freedom of the k^{th} dipole, changing its *internal* energy E_k : $dE_k = d\mathcal{W}_k$. This energy change may be viewed as coming from the dipole's potential energy in the field: $dE_k = -dU_k$.

⁸ Here, as in all my series, I am using the SI units; for their conversion to the Gaussian units, I have to refer the reader to the EM part of the series.

⁹ Note that in systems of discrete particles, most generalized forces including the fields \mathcal{E} and \mathcal{H} , differ from the mechanical pressure P in the sense that their work may be explicitly partitioned into single-particle components – see Eqs. (2b) and (3b). This fact gives some discretion for the approaches based on thermodynamic potentials – see Sec.4 below.

¹⁰ The notion of entropy was introduced into thermodynamics in 1865 by Rudolf Julius Emanuel Clausius on a purely phenomenological basis. In the absence of a clear understanding of entropy's microscopic origin (which had to wait for the works by L. Boltzmann and J. Maxwell), this was an amazing intellectual achievement.

second thought, the irreversibility is rather surprising, taking into account that the “microscopic” laws governing the motion of the system’s components are *time-reversible* – such as Newton’s laws or the basic laws of quantum mechanics.¹¹ Indeed, if at a late stage of the diffusion process, we reversed the velocities of all molecules exactly and simultaneously, the ink molecules would again gather (for a moment) into the original spot.¹² The problem is that getting the *information* necessary for the exact velocity reversal is not practicable.

A quantitative discussion of the reversibility-irreversibility dilemma requires a strict definition of the basic notion of statistical mechanics (and indeed of the probability theory): the *statistical ensemble*, and I would like to postpone it until the beginning of Chapter 2. In particular, in that chapter, we will see that the basic law of irreversible behavior is a growth or constancy of the entropy S in any closed system. Thus, the statistical mechanics, without defying the “microscopic” laws governing the evolution of the system’s components, introduces on top of them some new “macroscopic” laws, intrinsically related to *information*, i.e. the depth of our knowledge of the microscopic state of the system.

To conclude this brief discussion of variables, let me mention that as in all fields of physics, a very special role in statistical mechanics is played by the *energy* E . To emphasize the commitment to disregard the motion of the system as a whole in this subfield of physics, the E considered in thermodynamics it is frequently called the *internal energy*, though just for brevity, I will skip this adjective in most cases. The simplest example of such E is the sum of kinetic energies of molecules in a dilute gas at their thermal motion, but in general, the internal energy also includes not only the individual energies of the system’s components but also their interactions with each other. Besides a few “pathological” cases of very-long-range interactions, the interactions may be treated as local; in this case, the internal energy is proportional to N , i.e. is an extensive variable. As will be shown below, other extensive variables with the dimension of energy are often very useful as well, including the (Helmholtz) *free energy* F , the *Gibbs energy* G , the *enthalpy* H , and the *grand potential* Ω . (The collective name for such variables is *thermodynamic potentials*.)

Now, we are ready for a brief discussion of the relationship between *statistical physics* and *thermodynamics*. While the task of statistical physics is to calculate the macroscopic variables discussed above¹³ for various microscopic models of the system, the main role of thermodynamics is to derive some general relations between the average values of the macroscopic variables (also called *thermodynamic variables*) that do not depend on specific models. Surprisingly, it is possible to accomplish such a feat using just a few either evident or very plausible general assumptions (sometimes called the *laws of thermodynamics*), which find their proofs in statistical physics.¹⁴ Such general relations allow for a substantial reduction of the number of calculations we have to do in statistical physics: in most cases, it is sufficient to calculate from the statistics just one or two variables, and then

¹¹ Because of that, the possibility of the irreversible macroscopic behavior of microscopically reversible systems was questioned by some serious scientists as recently as in the late 19th century – notably by J. Loschmidt in 1876.

¹² While quantum-mechanical effects, with their intrinsic uncertainty, may be quantitatively important in this example, our qualitative discussion does not depend on them.

¹³ Several other important quantities, for example the heat capacity C , may be calculated as partial derivatives of the basic variables discussed above. Also, at certain conditions, the number of particles N in a system cannot be fixed and should also be considered as an (extensive) variable – see Sec. 5 below.

¹⁴ Admittedly, some of these proofs are based on other plausible but deeper postulates, for example, the central statistical hypothesis (see Sec. 2.2 below) whose best proof, to my knowledge, is just the whole body of experimental data.

use thermodynamic relations to get all other properties of interest. Thus the science of thermodynamics, sometimes snubbed as a phenomenology, deserves every respect not only as a useful theoretical tool but also as a discipline more general than any particular statistical model. This is why the balance of this chapter is devoted to a brief review of thermodynamics.

1.2. The 2nd law of thermodynamics, entropy, and temperature

Thermodynamics accepts a phenomenological approach to the entropy S , by postulating that there is such a unique extensive measure of the aggregate disorder and that in a *closed system* (defined as a system completely isolated from its environment, i.e. the system with its internal energy fixed), it may only grow in time, reaching its constant (maximum) value at equilibrium:¹⁵

$$dS \geq 0. \quad (1.4)$$

2nd law of
thermo-
dynamics

This postulate is called the *2nd law of thermodynamics* – arguably its only substantial new law.^{16,17}

This law, together with the additivity of S (as an extensive variable) in composite systems of non-interacting parts is sufficient for a formal definition of temperature, and a derivation of its basic properties that comply with our everyday notion of this key variable. Indeed, let us consider a closed system consisting of two fixed-volume subsystems (Fig. 2) whose internal relaxation is very fast in comparison with the rate of the thermal flow (i.e. the energy and entropy exchange) between the parts. In this case, on the latter time scale, each part is always in a quasistatic state, which may be described by a unique relation $E(S)$ between its energy and entropy.¹⁸

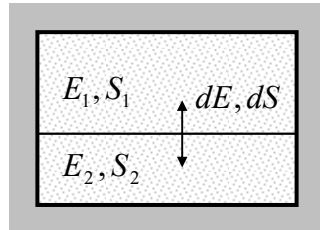


Fig. 1.2. A. composite thermodynamic system.

Neglecting the energy of interaction between the parts (which is always possible at $N \gg 1$, and in the absence of very-long-range interactions), we may use the extensive character of the variables E and S to write

$$E = E_1(S_1) + E_2(S_2), \quad S = S_1 + S_2, \quad (1.5)$$

for the full energy and entropy of the system. Now let us use them to calculate the following derivative:

¹⁵ Implicitly, this statement also postulates the existence, in a closed system, of *thermodynamic equilibrium*, an asymptotically reached state in which all macroscopic variables, including entropy, remain constant. Sometimes this postulate is called the *0th law of thermodynamics*.

¹⁶ Two initial formulations of this law, which were later proved equivalent, had been put forward independently by Lord Kelvin (born William Thomson) in 1851 and by Rudolf Clausius in 1854.

¹⁷ Note that according to Eq. (4), a macroscopically reversible process is possible only when the net entropy (of the system under consideration plus its environment involved in the process) does not change.

¹⁸ Here we strongly depend on a very important (and possibly the least intuitive) aspect of the 2nd law, namely that entropy is a *unique* macroscopic measure of disorder.

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} \equiv \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{d(E - E_1)}{dE_1}. \quad (1.6)$$

Since the total energy E of the closed system is fixed and hence independent of its re-distribution between the subsystems, we have to take $dE/dE_1 = 0$, and Eq. (6) yields

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2}. \quad (1.7)$$

According to the 2nd law of thermodynamics, when the two parts have reached the thermodynamic equilibrium, the total entropy S reaches its maximum, so $dS/dE_1 = 0$, and Eq. (7) yields

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2}. \quad (1.8)$$

This equality shows that if a thermodynamic system may be partitioned into weakly interacting macroscopic parts, their derivatives dS/dE should be equal in equilibrium. The reciprocal of this derivative is called *temperature*. Taking into account that our analysis pertains to the situation (Fig. 2) when both volumes $V_{1,2}$ are fixed, we may write this definition as

$$\left(\frac{\partial E}{\partial S} \right)_V \equiv T, \quad (1.9) \quad \text{Definition of temperature}$$

the subscript V meaning that volume is kept constant at the differentiation. (Such notation is common and very useful in thermodynamics, with its broad range of variables.)

Note that according to Eq. (9), if the temperature is measured in energy units¹⁹ (as I will do in this course for the brevity of notation), then S is dimensionless. The transfer to the SI or Gaussian units, i.e. to the temperature T_K measured in kelvins (not “Kelvins”, and not “degrees Kelvin”, please!), is given by the relation $T = k_B T_K$, where the *Boltzmann constant* $k_B \approx 1.38 \times 10^{-23} \text{ J/K} = 1.38 \times 10^{-16} \text{ erg/K}$.²⁰ In those units, the entropy becomes dimensional: $S_K = k_B S$.

The definition of temperature given by Eq. (9), is of course in sharp contrast with the popular notion of T as a measure of the average energy of one particle. However, as we will repeatedly see below, in many cases these two notions may be reconciled, with Eq. (9) being more general. In particular, the so-defined T is in agreement with our everyday notion of temperature.²¹

(i) according to Eq. (9), the temperature is an intensive variable (since both E and S are extensive), i.e., in a system of similar particles, it is independent of the particle number N ;

¹⁹ Here I have to mention a traditional unit of thermal energy, the calorie, still being used in some applied fields. In the most common modern definition (as the so-called *thermochemical calorie*) it equals exactly 4.148 J.

²⁰ For the more exact values of this and other constants, see appendix *UCA: Selected Units and Constants*. Note that both T and T_K define the natural *absolute* (also called “thermodynamic”) *scale* of temperature, vanishing at the same point – in contrast to such artificial scales as the degrees Celsius (“centigrades”), defined as $T_C \equiv T_K + 273.15$, or the degrees Fahrenheit: $T_F \equiv (9/5)T_C + 32$.

²¹ Historically, this notion was initially only qualitative – just as something distinguishing “hot” from “cold”. After the invention of thermometers (the first one by Galileo Galilei in 1592), mostly based on the thermal expansion of fluids, this notion had become quantitative but not very deep: being understood as something “what thermometers measure” – until its physical sense as a measure of thermal motion’s intensity, was revealed in the 19th century.

- (ii) temperatures of all parts of a system are equal at equilibrium – see Eq. (8);
- (iii) in a closed system whose parts are *not* in equilibrium, thermal energy (*heat*) always flows from the warmer part (with a higher T) to the colder part.

In order to prove the last property, let us revisit the closed composite system shown in Fig. 2, and consider another derivative:

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} \equiv \frac{dS_1}{dE_1} \frac{dE_1}{dt} + \frac{dS_2}{dE_2} \frac{dE_2}{dt}. \quad (1.10)$$

If the internal state of each part is very close to equilibrium (as was assumed from the very beginning) at each moment of time, we can use Eq. (9) to replace the derivatives $dS_{1,2}/dE_{1,2}$ with $1/T_{1,2}$, getting

$$\frac{dS}{dt} = \frac{1}{T_1} \frac{dE_1}{dt} + \frac{1}{T_2} \frac{dE_2}{dt}. \quad (1.11)$$

Since in a closed system $E = E_1 + E_2 = \text{const}$, these time derivatives are related as $dE_2/dt = -dE_1/dt$, and Eq. (11) yields

$$\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt}. \quad (1.12)$$

But according to the 2nd law of thermodynamics, this derivative cannot be negative: $dS/dt \geq 0$. Hence,

$$\left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \geq 0. \quad (1.13)$$

For example, if $T_1 > T_2$, then $dE_1/dt \leq 0$, i.e. the warmer part gives energy to its colder counterpart.

Note also that such a heat exchange, at fixed volumes $V_{1,2}$, and $T_1 \neq T_2$, increases the total system's entropy, without performing any "useful" mechanical work – see Eq. (1).

1.3. The 1st and 3rd laws of thermodynamics, and heat capacity

First, let us consider a *thermally* insulated system whose volume V may be changed by force – see, for example, Fig. 1. Such a system is different from the fully closed one, because its energy E may be changed by the external force's work – see Eq. (1):

$$dE = d\mathcal{W} = -PdV. \quad (1.14)$$

Let the volume change be not only quasistatic but also static-friction-free (reversible), so the system is virtually at equilibrium at any instant. Such a reversible process, in the particular case of a thermally insulated system, is also called *adiabatic*. If the pressure P (or any generalized external force \mathcal{F}_j) is deterministic, i.e. is a predetermined function of time, independent of the state of the system under analysis, it may be considered as coming from a fully ordered system, i.e. the one with zero entropy, with the aggregate system (consisting of the system under our analysis plus the source of the force) completely closed. Since the entropy of the total closed system should stay constant (see the second of Eqs. (5) above), the S of the system under analysis should stay constant on its own. Thus we arrive at a very important conclusion: at an adiabatic process in a system, its entropy cannot change. (Sometimes such a process is called *isentropic*.) This means that we may use Eq. (14) to write

$$P = -\left(\frac{\partial E}{\partial V}\right)_S. \quad (1.15)$$

Now let us consider a more general thermodynamic system that may also exchange thermal energy (“heat”) with its environment (Fig. 3).

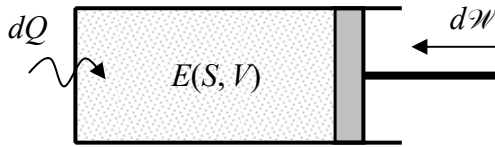


Fig. 1.3. An example of the thermodynamic process involving both the mechanical work by the environment and the heat exchange with it.

For such a system, our previous conclusion about the entropy’s constancy is not valid, so in equilibrium, S may be a function of not only the system’s energy E but also of its volume: $S = S(E, V)$. Let us consider this relation resolved for energy: $E = E(S, V)$, and write the general mathematical expression for the full differential of E as a function of these two independent arguments:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV. \quad (1.16)$$

This formula, based on the stationary relation $E = E(S, V)$, is evidently valid not only in equilibrium but also for all reversible²² processes. Now, using Eqs. (9) and (15), we may rewrite Eq. (16) as

$$dE = TdS - PdV. \quad (1.17)$$

Energy:
differential

According to Eq. (1), the second term on the right-hand side of this equation is just the work of the external force, so due to the conservation of energy,²³ the first term has to be equal to the *heat* dQ transferred from the environment to the system (see Fig. 3):

$$dE = dQ + d\mathcal{W}, \quad (1.18)$$

$$dQ = TdS. \quad (1.19)$$

1st law of
thermo-
dynamics

The last relation, divided by T and then integrated along an arbitrary (but reversible!) process,

$$S = \int \frac{dQ}{T} + \text{const}, \quad (1.20)$$

is sometimes used as an alternative definition of entropy S – provided that temperature is defined not by Eq. (9), but in some independent way. It is useful to recognize that entropy (like energy) may be defined

²² Let me emphasize again that any adiabatic process is reversible, but not vice versa.

²³ Such conservation, expressed by Eqs. (18)-(19), is commonly called the *1st law of thermodynamics*. While it (in contrast with the 2nd law) does not present any new law of nature, and in particular was already used de-facto to write the first of Eqs. (5) and also Eq. (14), such a grand name was absolutely justified in the early 19th century when the mechanical nature of internal energy (including the motion of atoms and molecules) was not at all clear. In this context, the names of at least three great scientists: Benjamin Thompson (who gave, in 1799, convincing arguments that heat cannot be anything but a form of particle motion), Julius Robert von Mayer (who conjectured the conservation of the sum of the thermal and macroscopic mechanical energies in 1841), and James Prescott Joule (who proved this conservation experimentally two years later), have to be reverently mentioned.

only to an arbitrary constant, which does not affect any other thermodynamic observables. The common convention is to take

$$S \rightarrow 0, \quad \text{at } T \rightarrow 0. \quad (1.21)$$

This condition is sometimes called the “3rd law of thermodynamics”, but it is important to realize that this is just a convention rather than a real law.²⁴ Indeed, the convention corresponds well to the notion of the full order at $T = 0$ in some systems (e.g., separate atoms or perfect crystals), but creates ambiguity for other systems, e.g., amorphous solids (like the usual glasses) that may remain highly disordered for “astronomic” times, even at $T \rightarrow 0$.

Now let us discuss the notion of *heat capacity* that, by definition, is the ratio dQ/dT , where dQ is the amount of heat that should be given to a system to raise its temperature by a small amount dT .²⁵ (This notion is important because the heat capacity may be most readily measured experimentally.) The heat capacity depends, naturally, on whether the heat dQ goes only into an increase of the internal energy dE of the system (as it does if its volume V is constant), or also into the mechanical work ($-d\mathcal{W}$) performed by the system at its expansion – as it happens, for example, if the pressure P , rather than the volume V , is fixed (the so-called *isobaric* process – see Fig. 4).

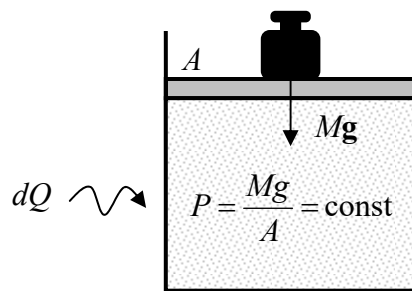


Fig. 1.4. The simplest example of the isobaric process.

Hence we should discuss at least two different quantities,²⁶ the *heat capacity at fixed volume*,

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V \quad (1.22)$$

Heat capacity: definitions
and the *heat capacity at fixed pressure*

$$C_P \equiv \left(\frac{\partial Q}{\partial T} \right)_P, \quad (1.23)$$

²⁴Actually, the 3rd law (also called the *Nernst theorem*) as postulated by Walter Hermann Nernst in 1912 was different – and really meaningful: “It is impossible for any procedure to lead to the isotherm $T = 0$ in a finite number of steps.” I will discuss this theorem at the end of Sec. 6.

²⁵ By this definition, the full heat capacity of a system is an extensive variable, but it may be used to form such intensive variables as the heat capacity per particle, called the *specific heat capacity*, or just the *specific heat*. (Please note that the last terms are rather ambiguous: they are also used for the heat capacity per unit mass and per unit volume, so some caution is in order.)

²⁶ Dividing both sides of Eq. (19) by dT , we get the general relation $dQ/dT = TdS/dT$, which may be used to rewrite the definitions (22) and (23) in the following forms:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad C_P = T \left(\frac{\partial S}{\partial T} \right)_P,$$

which are more convenient for some applications.

and expect that for all “normal” (mechanically stable) systems, $C_P \geq C_V$. The difference between C_P and C_V is minor for most liquids and solids, but may be very substantial for gases – see the next section.

1.4. Thermodynamic potentials

Since for a fixed volume, $d\mathcal{W} = -PdV = 0$ and Eq. (18) yields $dQ = dE$, we may rewrite Eq. (22) in another convenient form

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V. \quad (1.24)$$

so to calculate C_V from a certain statistical-physics model, we only need to calculate E as a function of temperature and volume. If we want to obtain a similarly convenient expression for C_P , the best way is to introduce a new notion of so-called *thermodynamic potentials* – whose introduction and effective use is perhaps one of the most impressive techniques of thermodynamics. For that, let us combine Eqs. (1) and (18) to write the 1st law of thermodynamics in its most common form

$$dQ = dE + PdV. \quad (1.25)$$

At an isobaric process (Fig. 4), i.e. at $P = \text{const}$, this expression is reduced to

$$(dQ)_P = dE_P + d(PV)_P = d(E + PV)_P. \quad (1.26)$$

Thus, if we introduce a new function with the dimensionality of energy:²⁷

$$H \equiv E + PV, \quad (1.27)$$

Enthalpy:
definition

called *enthalpy* (or, sometimes, the “heat function” or the “heat contents”),²⁸ we may rewrite Eq. (23) as

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (1.28)$$

Comparing Eqs. (28) and (24), we see that for the heat capacity, the enthalpy H plays the same role at fixed pressure as the internal energy E plays at fixed volume.

Now let us explore the enthalpy’s properties at an *arbitrary* reversible process, lifting the restriction $P = \text{const}$, but keeping the definition (27). Differentiating this equality, we get

$$dH = dE + PdV + VdP. \quad (1.29)$$

Plugging into this relation Eq. (17) for dE , we see that the terms $\pm PdV$ cancel, yielding a very simple expression

$$dH = TdS + VdP, \quad (1.30)$$

Enthalpy:
differential

whose right-hand side differs from Eq. (17) only by the swap of P and V in the second term, with the simultaneous change of its sign. Formula (30) shows that if H has been found (say, experimentally

²⁷ From the point of view of mathematics, Eq. (27) is a particular case of the so-called *Legendre transformations*.

²⁸ This function (as well as the Gibbs free energy G , see below), had been introduced in 1875 by J. Gibbs, though the term “enthalpy” was coined (much later) by H. Onnes.

measured or calculated for a certain microscopic model) as a function of the entropy S and the pressure P of a system, we can calculate its temperature T and volume V by simple partial differentiation:

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad V = \left(\frac{\partial H}{\partial P} \right)_S. \quad (1.31)$$

The comparison of the first of these relations with Eq. (9) shows that not only for the heat capacity but for the temperature as well, at fixed pressure, enthalpy plays the same role as played by internal energy at fixed volume.

This success immediately raises the question of whether we could develop this idea further on, by defining other useful thermodynamic potentials – the variables with the dimensionality of energy that would have similar properties – first of all, a potential that would enable a similar swap of T and S in its full differential, in comparison with Eq. (30). We already know that an adiabatic process is a reversible process with constant *entropy*, inviting analysis of a reversible process with constant *temperature*. Such an *isothermal process* may be implemented, for example, by placing the system under consideration into thermal contact with a much larger system (called either the *heat bath*, or “heat reservoir”, or “thermostat”) that remains in thermodynamic equilibrium at all times – see Fig. 5.

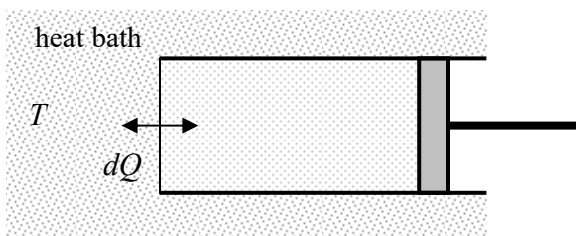


Fig. 1.5. The simplest example of the isothermal process.

Due to its very large size, the heat bath’s temperature T does not depend on what is being done with our system. If the change is being done sufficiently slowly (i.e. reversibly), this temperature is also the temperature of our system – see Eq. (8) and its discussion. Let us calculate the elementary mechanical work $d\mathcal{W}$ (1) at such a reversible isothermal process. According to the general Eq. (18), $d\mathcal{W} = dE - dQ$. Plugging dQ from Eq. (19) into this equality, for $T = \text{const}$ we get

$$(d\mathcal{W})_T = dE - TdS = d(E - TS) \equiv dF, \quad (1.32)$$

where the following combination,

Free energy:
definition

$$F \equiv E - TS, \quad (1.33)$$

is called the *free energy* (or the “Helmholtz free energy”, or just the “Helmholtz energy”²⁹). Just as we have done for the enthalpy, let us establish properties of this new thermodynamic potential for an arbitrarily small, reversible (now not necessarily isothermal!) variation of variables, while keeping the definition (33). Differentiating this relation and then using Eq. (17), we get

Free energy:
differential

$$dF = -SdT - PdV. \quad (1.34)$$

²⁹ It was named after Hermann von Helmholtz (1821-1894). The last of the listed terms for F was recommended by the most recent (1988) IUPAC decision, but I will use the first term, which prevails in the physics literature. The origin of the adjective “free” stems from Eq. (32): F may be interpreted as the internal energy’s part that is “free” to be transferred to the mechanical work, at the (very common) isothermal process.

Thus, if we know the function $F(T, V)$, we can calculate S and P by simple differentiation:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \quad (1.35)$$

Now we may notice that the system of all partial derivatives may be made full and symmetric if we introduce one more thermodynamic potential. Indeed, we have already seen that each of the three already introduced thermodynamic potentials (E , H , and F) has an especially simple full differential if it is considered as a function of its two *canonical* arguments: one of the “thermal variables” (either S or T) and one of the “mechanical variables” (either P or V):³⁰

$$E = E(S, V); \quad H = H(S, P); \quad F = F(T, V). \quad (1.36)$$

In this list of pairs of four arguments, only one pair is missing: $\{T, P\}$. The thermodynamic function of this pair, which gives the two remaining variables (S and V) by simple differentiation, is called the *Gibbs energy* (or sometimes the “Gibbs free energy”): $G = G(T, P)$. The way to define it in a symmetric fashion is evident from the so-called *circular diagram* shown in Fig. 6.

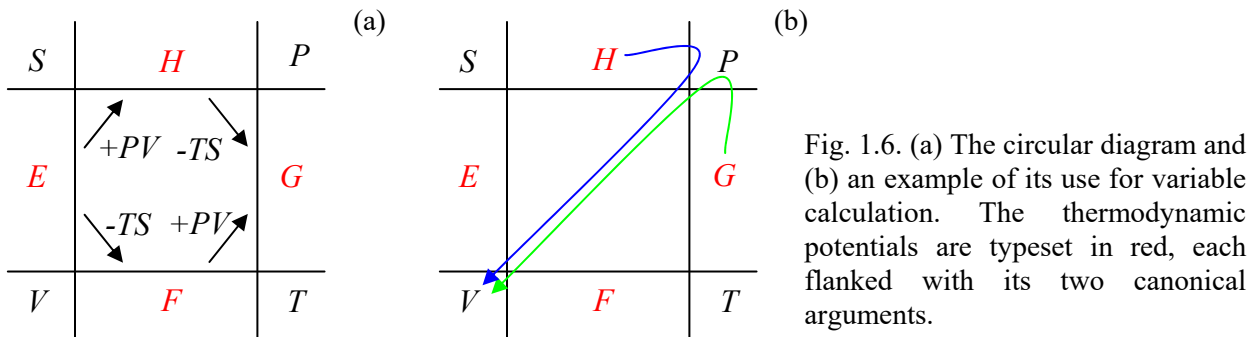


Fig. 1.6. (a) The circular diagram and (b) an example of its use for variable calculation. The thermodynamic potentials are typeset in red, each flanked with its two canonical arguments.

In this diagram, each thermodynamic potential is placed between its two canonical arguments – see Eq. (36). The left two arrows in Fig. 6a show the way the potentials H and F have been obtained from energy E – see Eqs. (27) and (33). This diagram hints that G has to be defined as shown by either of the two right arrows on that panel, i.e. as

$$G \equiv F + PV \equiv H - TS \equiv E - TS + PV. \quad (1.37)$$

Gibbs energy: definition

In order to verify this idea, let us calculate the full differential of this new thermodynamic potential, using, e.g., the first form of Eq. (37) together with Eq. (34):

$$dG = dF + d(PV) = (-SdT - PdV) + (PdV + VdP) \equiv -SdT + VdP, \quad (1.38)$$

Gibbs energy: differential

so if we know the function $G(T, P)$, we can indeed readily calculate both entropy and volume:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T. \quad (1.39)$$

³⁰ Note the similarity of this situation with that in analytical mechanics (see, e.g., CM Chapters 2 and 10): the Lagrangian function may be used for a simple derivation of the equations of motion if it is expressed as a function of generalized coordinates and their *velocities*, while to use the Hamiltonian function in a similar way, it has to be expressed as a function of the generalized coordinates and the corresponding *momenta*.

The circular diagram completed in this way is a good mnemonic tool for recalling Eqs. (9), (15), (31), (35), and (39), which express thermodynamic variables as partial derivatives of the thermodynamic potentials. Indeed, the variable in any corner of the diagram may be found as a partial derivative of any of two potentials that are not its direct neighbors, over the variable in the opposite corner. For example, the green line in Fig. 6b corresponds to the second of Eqs. (39), while the blue line, to the second of Eqs. (31). At this procedure, all the derivatives giving the variables of the upper row (S and P) have to be taken with negative signs, while those giving the variables of the bottom row (V and T), with positive signs.³¹

Now I have to justify the collective name “thermodynamic potentials” used for E , H , F , and G . For that, let us consider a *macroscopically irreversible* process, for example, direct thermal contact of two bodies with different initial temperatures. As was discussed in Sec. 2, at such a process, the entropy may grow even without the external heat flow: $dS \geq 0$ at $dQ = 0$ – see Eq. (12). This means that at a more general process with $dQ \neq 0$, the entropy may grow faster than predicted by Eq. (19), which has been derived for a reversible process, so

$$dS \geq \frac{dQ}{T}, \quad (1.40)$$

with the equality approached in the reversible limit. Plugging Eq. (40) into Eq. (18) (which, being just the energy conservation law, remains valid for irreversible processes as well), we get

$$dE \leq TdS - PdV. \quad (1.41)$$

We can use this relation to have a look at the behavior of other thermodynamic potentials in irreversible situations, still keeping their definitions given by Eqs. (27), (33), and (37). Let us start from the (very common) case when both the temperature T and the volume V of a system are kept constant. If the process is reversible, then according to Eq. (34), the full time derivative of the free energy F would equal zero. Eq. (41) says that in an irreversible process, this is not necessarily so: if $dT = dV = 0$, then

$$\frac{dF}{dt} = \frac{d}{dt}(E - TS)_T = \frac{dE}{dt} - T \frac{dS}{dt} \leq 0. \quad (1.42)$$

Hence, in the general (irreversible) situation, F can only decrease, but not increase in time. This means that F eventually approaches its minimum value $F(T, V)$ given by the equations of reversible thermodynamics. To re-phrase this important conclusion, in the case $T = \text{const}$ and $V = \text{const}$, the free energy F , i.e. the difference $E - TS$, plays the role of the potential energy in the classical mechanics of dissipative processes: its minimum corresponds to the (in the case of F , thermodynamic) equilibrium of the system. This is one of the key results of thermodynamics, and I invite the reader to give it some thought. One of its possible handwaving interpretations of this fact is that the heat bath with fixed $T > 0$, i.e. with a substantial thermal agitation of its components, “wants” to impose thermal disorder in the system immersed into it, by “rewarding” it with lower F for any increase of the disorder.

³¹ There is also a wealth of other relations between thermodynamic variables that may be represented as second derivatives of the thermodynamic potentials, including four *Maxwell relations* such as $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, etc. (They may be readily recovered from the well-known property of a function of two independent arguments, say, $f(x, y)$: $\partial(\partial f/\partial x)/\partial y = \partial(\partial f/\partial y)/\partial x$.) In this chapter, I will list only the thermodynamic relations that will be used later in the course; a more complete list may be found, e.g., in Sec. 16 of the book by L. Landau and E. Lifshitz, *Statistical Physics, Part 1*, 3rd ed., Pergamon, 1980 (and its later re-printings).

Repeating the calculation for a different case, $T = \text{const}$, $P = \text{const}$, it is easy to see that in this case the same role is played by the Gibbs energy:

$$\frac{dG}{dt} \equiv \frac{d}{dt}(E - TS + PV) = \frac{dE}{dt} - T \frac{dS}{dt} + P \frac{dV}{dt} \leq (T \frac{dS}{dt} - P \frac{dV}{dt}) - T \frac{dS}{dt} + P \frac{dV}{dt} \equiv 0, \quad (1.43)$$

so the thermal equilibrium now corresponds to the minimum of G rather than F .

For the two remaining thermodynamic potentials, E and H , calculations similar to Eqs. (42) and (43) are possible but make less sense because that would require keeping $S = \text{const}$ (with $V = \text{const}$ for E , and $P = \text{const}$ for H) for an irreversible process, but it is usually hard to prevent the entropy from growing if initially it had been lower than its equilibrium value, at least on the long-term basis.³² Thus physically, the circular diagram is not so symmetric after all: G and F are somewhat more useful for most practical calculations than E and H .

Note that the difference $G - F = PV$ between the two “more useful” potentials has very little to do with thermodynamics at all because this difference exists (although is not much advertised) in classical mechanics as well.³³ Indeed, the difference may be generalized as $G - F = -\mathcal{F}q$, where q is a generalized coordinate, and \mathcal{F} is the corresponding generalized force. The minimum of F corresponds to the equilibrium of an autonomous system (with $\mathcal{F} = 0$), while the equilibrium position of the same system under the action of external force \mathcal{F} is given by the minimum of G . Thus the external force “wants” the system to subdue to its effect, “rewarding” it with lower G .

Moreover, the difference between F and G becomes a bit ambiguous (approach-dependent) when the product $\mathcal{F}q$ may be partitioned into single-particle components – just as it is done in Eqs. (2b) and (3b) for the electric and magnetic fields. Here the applied field may be taken into account on the microscopic level, by including its effect directly into the energy ε_k of each particle. In this case, the field contributes to the total internal energy E directly, and hence the thermodynamic equilibrium (at $T = \text{const}$) is described as the minimum of F . (We may say that in this case $F = G$, unless a difference between these thermodynamic potentials is created by the actual mechanical pressure P .) However, in some cases, typically for condensed systems with their strong interparticle interactions, the easier (and sometimes the only practicable³⁴) way to account for the field is on the macroscopic level, by taking $G = F - \mathcal{F}q$. In this case, the same equilibrium state is described as the minimum of G . Several examples of this dichotomy will be given later in this course. Whatever the choice, one has to be careful not to take the same field effect into account twice.

³² There are a few practicable systems, notably including the so-called *adiabatic magnetic refrigerators* (to be discussed in Chapter 2), where the unintentional growth of S is so slow that the condition $S = \text{const}$ may be closely approached during a finite but substantial time interval.

³³ It is convenient to describe it as the difference between the “usual” (internal) potential energy U of the system to its “Gibbs potential energy” U_G – see CM Sec. 1.4. For the readers who skipped that discussion: my pet example is the usual elastic spring with $U = kx^2/2$, under the effect of an external force \mathcal{F} , whose equilibrium position ($x_0 = \mathcal{F}/k$) evidently corresponds to the minimum of $U_G = U - \mathcal{F}x$, rather than just U .

³⁴ An example of such an extreme situation is the case when an external magnetic field \mathcal{H} is applied to a macroscopic sample of a type-1 superconductor in its so-called *intermediate state*, in which the sample partitions into domains of the “normal” phase with $\mathcal{B} = \mu_0 \mathcal{H}$, and the superconducting phase with $\mathcal{B} = 0$. (For more on this topic see, e.g., EM Secs. 6.4-6.5.) In this case, the field is effectively applied to the interfaces between the domains, very similarly to the mechanical pressure applied to a gas portion via a piston – see Fig. 1 again.

One more important conceptual question I would like to discuss here is why usually statistical physics pursues the calculation of thermodynamic potentials rather than just of a relation between P , V , and T . (Such relation is called the *equation of state* of the system.) Let us explore this issue on the particular but very important example of an *ideal classical gas* in thermodynamic equilibrium, for which the equation of state should be well known to the reader from undergraduate physics:³⁵

$$PV = NT, \quad (1.44)$$

where N is the number of particles in volume V . (In Chapter 3, we will derive Eq. (44) from statistics.) Let us try to use it for the calculation of all thermodynamic potentials, and all other thermodynamic variables discussed above. We may start, for example, from the calculation of the free energy F . Indeed, integrating the second of Eqs. (35), with the pressure calculated from Eq. (44): $P = NT/V$, we get

$$F = -\int PdV|_{T=\text{const}} = -NT \int \frac{dV}{V} \equiv -NT \int \frac{d(V/N)}{(V/N)} = -NT \ln \frac{V}{N} + Nf(T), \quad (1.45)$$

where V has been divided by N in both instances just to represent F as a manifestly extensive variable, in this uniform system proportional to N . The integration “constant” $f(T)$ is some function of temperature, which cannot be recovered from the equation of state. This function affects all other thermodynamic potentials, and the entropy as well. Indeed, by using the first of Eqs. (35) together with Eq. (45), we get

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N \left[\ln \frac{V}{N} - \frac{df(T)}{dT} \right], \quad (1.46)$$

and now may combine Eqs. (33) with (46) to calculate the (internal) energy of the gas,³⁶

$$E = F + TS = \left[-NT \ln \frac{V}{N} + Nf(T) \right] + T \left[N \ln \frac{V}{N} - N \frac{df(T)}{dT} \right] \equiv N \left[f(T) - T \frac{df(T)}{dT} \right]. \quad (1.47)$$

From here, we may use Eqs. (27), (44), and (47) to calculate the gas’ enthalpy,

$$H = E + PV = E + NT = N \left[f(T) - T \frac{df(T)}{dT} + T \right], \quad (1.48)$$

and, finally, plug Eqs. (44) and (45) into Eq. (37) to calculate its Gibbs energy

$$G = F + PV = N \left[-T \ln \frac{V}{N} + f(T) + T \right]. \quad (1.49)$$

³⁵ The long history of the gradual discovery of this relation includes the very early (circa 1662) work by R. Boyle and R. Townely, followed by contributions from H. Power, E. Mariotte, J. Charles, J. Dalton, and J. Gay-Lussac. It was fully formulated by Benoît Paul Émile Clapeyron in 1834, in the form $PV = nRT_K$, where n is the number of moles in the gas sample, and $R \approx 8.31 \text{ J/mole}\cdot\text{K}$ is the so-called *gas constant*. This form is equivalent to Eq. (44), taking into account that $R \equiv k_B N_A$, where $N_A = 6.022 \ 140 \ 76 \times 10^{23} \text{ mole}^{-1}$ is the *Avogadro number*, i.e. the number of molecules per mole. (By the mole’s definition, N_A is just the reciprocal mass, in grams, of the $1/12^{\text{th}}$ part of the ^{12}C atom, which is close to the masses of one proton or one neutron – see *Appendix UCA: Selected Units and Constants*.) Historically, this equation of state was the main argument for the introduction of the absolute temperature T , because only with it, the equation acquires the spectacularly simple form (44).

³⁶ Note that Eq. (47), in particular, describes a very important property of the ideal classical gas: its energy depends only on temperature (and the number of particles), but not on volume or pressure.

One might ask whether the function $f(T)$ is physically significant, or it is something like the inconsequential, arbitrary constant – like the one that may be always added to the potential energy in non-relativistic mechanics. In order to address this issue, let us calculate, from Eqs. (24) and (28), both heat capacities, which are evidently measurable quantities:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = -NT \frac{d^2 f}{dT^2}, \quad (1.50)$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = N \left(-T \frac{d^2 f}{dT^2} + 1 \right) = C_V + N. \quad (1.51)$$

We see that the function $f(T)$, or at least its second derivative, is measurable.³⁷ (In Chapter 3, we will calculate this function for two simple “microscopic” models of the ideal classical gas.) The meaning of this function is evident from the physical picture of the ideal gas: the pressure P exerted on the walls of the containing volume is produced only by the translational motion of the gas molecules, while their internal energy E (and hence other thermodynamic potentials) may be also contributed by the internal dynamics of the molecules – their rotation, vibration, etc. Thus, the equation of state does *not* give us the full thermodynamic description of a system, while the thermodynamic potentials do.

1.5. Systems with a variable number of particles

Now we have to consider one more important case: when the number N of particles in a system is not rigidly fixed but may change as a result of a thermodynamic process. A typical example of such a system is a gas sample separated from the environment by a penetrable partition – see Fig. 7.³⁸

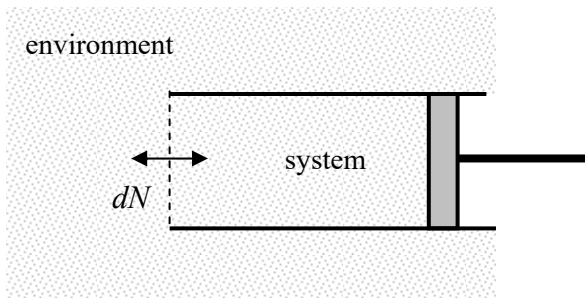


Fig. 1.7. An example of a system with a variable number of particles.

Let us analyze this situation in the simplest case when all the particles are similar. (In Sec. 4.1, this analysis will be extended to systems with particles of several sorts). In this case, we may consider N as an independent thermodynamic variable whose variation may change the energy E of the system, so Eq. (17) (valid for a slow, reversible process) should now be generalized as

$$dE = TdS - PdV + \mu dN, \quad (1.52)$$

Chemical potential: definition

³⁷ Note, however, that the difference $C_P - C_V = N$ is independent of $f(T)$. (If the temperature is measured in kelvins, this relation takes a more familiar form $C_P - C_V = nR$.) It is straightforward (and hence left for the reader's exercise) to prove that the difference $C_P - C_V$ of *any* system is fully determined by its equation of state.

³⁸ Another important example is a gas in contact with an open-surface liquid or solid of similar molecules.

where μ is some new function of state, called the *chemical potential*.³⁹ Keeping the definitions of other thermodynamic potentials, given by Eqs. (27), (33), and (37) intact, we see that the expressions for their differentials should be generalized as

$$dH = TdS + VdP + \mu dN, \quad (1.53a)$$

$$dF = -SdT - PdV + \mu dN, \quad (1.53b)$$

$$dG = -SdT + VdP + \mu dN, \quad (1.53c)$$

so the chemical potential may be calculated as either of the following partial derivatives:⁴⁰

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} = \left(\frac{\partial H}{\partial N} \right)_{S,P} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (1.54)$$

Despite the formal similarity of all Eqs. (54), one of them is more consequential than the others. Indeed, the Gibbs energy G is the only thermodynamic potential that is a function of two *intensive* parameters, T and P . However, just as all thermodynamic potentials, G has to be *extensive*, so in a system of similar particles it has to be proportional to N :

$$G = Ng, \quad (1.55)$$

where g is some function of T and P . Plugging this expression into the last of Eqs. (54), we see that μ equals exactly this function, so

$$\mu = \frac{G}{N}, \quad (1.56)$$

μ as Gibbs
energy

i.e. the chemical potential is just the Gibbs energy per particle.

In order to demonstrate how vital the notion of chemical potential may be, let us consider the situation (parallel to that shown in Fig. 2) when a system consists of two parts, with equal pressure and temperature, that can exchange particles at a relatively slow rate (much slower than the speed of the internal relaxation of each part). Then we can write two equations similar to Eqs. (5):

$$N = N_1 + N_2, \quad G = G_1 + G_2, \quad (1.57)$$

where $N = \text{const}$, and Eq. (56) may be used to describe each component of G :

$$G = \mu_1 N_1 + \mu_2 N_2. \quad (1.58)$$

Plugging the N_2 expressed from the first of Eqs. (57), $N_2 = N - N_1$, into Eq. (58), we see that

$$\frac{dG}{dN_1} = \mu_1 - \mu_2, \quad (1.59)$$

so the minimum of G is achieved at $\mu_1 = \mu_2$. Hence, in the conditions of fixed temperature and pressure, i.e. when G is the appropriate thermodynamic potential, the chemical potentials of the system parts should be equal – the so-called *chemical equilibrium*.

³⁹ This name, of a historic origin, is misleading: as evident from Eq. (52), μ has a clear *physical* sense of the average energy cost of adding one more particle to a system with $N \gg 1$.

⁴⁰ Note that strictly speaking, Eqs. (9), (15), (31), (35), and (39) should be now generalized by adding another lower index, N , to the corresponding derivatives; I will just imply them being calculated at constant N .

Finally, later in the course, we will also run into several cases when the volume V of a system, its temperature T , and the chemical potential μ are all fixed. (The last condition may be readily implemented by allowing the system of our interest to exchange particles with an environment so large that its μ stays constant.) The thermodynamic potential appropriate for this case may be obtained by subtraction of the product μN from the free energy F , resulting in the so-called *grand thermodynamic* (or “Landau”) *potential*:

$$\Omega \equiv F - \mu N = F - \frac{G}{N} N \equiv F - G = -PV. \quad (1.60)$$

Grand potential: definition

Indeed, for a reversible process, the full differential of this potential is

$$d\Omega = dF - d(\mu N) = (-SdT - PdV + \mu dN) - (\mu dN + Nd\mu) = -SdT - PdV - Nd\mu, \quad (1.61)$$

Grand potential: differential

so if Ω has been calculated as a function of T , V , and μ , other thermodynamic variables may be found as

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \quad N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}. \quad (1.62)$$

Now acting exactly as we have done for other potentials, it is straightforward to prove that an irreversible process with fixed T , V , and μ , provides $d\Omega/dt \leq 0$, so the system’s equilibrium indeed corresponds to the minimum of its grand potential Ω . We will repeatedly use this fact in this course.

1.6. Thermal machines

In order to complete this brief review of thermodynamics, I cannot completely pass the topic of *thermal machines* – not because they will be studied much in this course, but mostly because of their practical and historic significance.⁴¹ Figure 8a shows the generic scheme of a thermal machine that may perform mechanical work on its environment (in our notation, equal to $-\mathcal{W}$) during each cycle of the expansion/compression of some “working gas”, by transferring different amounts of heat from a high-temperature heat bath (Q_H) and to the low-temperature bath (Q_L).

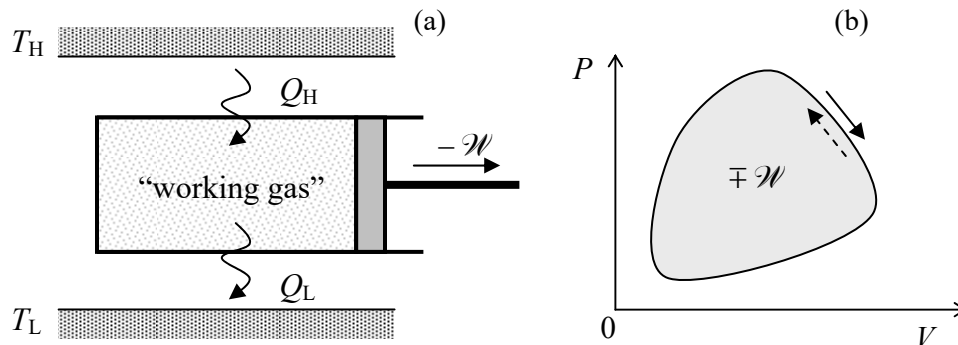


Fig. 1.8. (a) The simplest implementation of a thermal machine, and (b) the graphic representation of the mechanical work it performs. On panel (b), the solid arrow indicates the heat engine cycle direction, while the dashed arrow, the refrigerator cycle direction.

⁴¹ The whole field of thermodynamics was spurred by the famous 1824 work by Nicolas Léonard Sadi Carnot, in which he, in particular, gave an alternative, indirect form of the 2nd law of thermodynamics – see below.

One relation between the three amounts Q_H , Q_L , and \mathcal{W} is immediately given by the energy conservation (i.e. by the 1st law of thermodynamics):

$$Q_H - Q_L = -\mathcal{W}. \quad (1.63)$$

From Eq. (1), the mechanical work during the cycle may be calculated as

$$-\mathcal{W} = \oint PdV, \quad (1.64)$$

and hence represented by the area circumvented by the state-representing point on the $[P, V]$ plane – see Fig. 8b. Note that the sign of this circular integral depends on the direction of the point's rotation; in particular, the work ($-\mathcal{W}$) done by the working gas is positive at its clockwise rotation (pertinent to *heat engines*) and negative in the opposite case (implemented in *refrigerators* and *heat pumps* – see below). Evidently, the work depends on the exact form of the cycle, which in turn may depend not only on T_H and T_L but also on the working gas' properties.

An exception to this rule is the famous *Carnot cycle*, consisting of two isothermal and two adiabatic processes (all reversible!). In its heat engine's form, the cycle may start, for example, from an isothermic expansion of the working gas in contact with the hot bath (i.e. at $T = T_H$). It is followed by its additional adiabatic expansion (with the gas being disconnected from both heat baths) until its temperature drops to T_L . Then an isothermal compression of the gas is performed in its contact with the cold bath (at $T = T_L$), followed by its additional adiabatic compression to raise T to T_H again, after which the cycle is repeated again and again. Note that during this specific cycle, the working gas is never in contact with both heat baths simultaneously, thus avoiding the irreversible heat transfer between them. The cycle's shape on the $[V, P]$ plane (Fig. 9a) depends on the exact properties of the working gas and may be rather complicated. However, since the system's entropy is constant at any adiabatic process, the Carnot cycle's shape on the $[S, T]$ plane is always rectangular – see Fig. 9b.

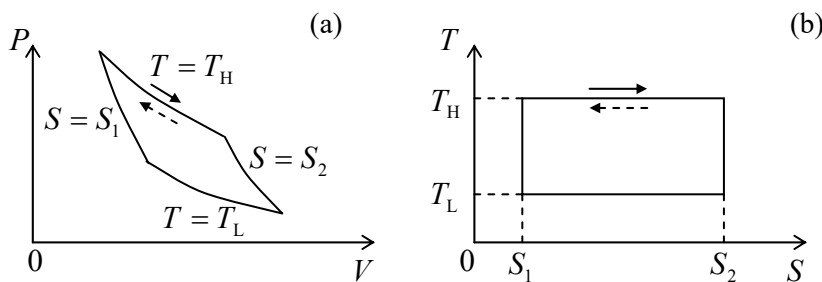


Fig. 1.9. Representations of the Carnot cycle: (a) on the $[V, P]$ plane (schematically), and (b) on the $[S, T]$ plane. The meaning of the arrows is the same as in Fig. 8.

Since during each isotherm, the working gas is brought into thermal contact only with the corresponding heat bath, i.e. its temperature is constant, the relation (19), $dQ = TdS$, may be immediately integrated to yield

$$Q_H = T_H(S_2 - S_1), \quad Q_L = T_L(S_2 - S_1). \quad (1.65)$$

Hence the ratio of these two heat flows is completely determined by their temperature ratio:

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}, \quad (1.66)$$

regardless of the working gas properties. Formulas (63) and (66) are sufficient to find the ratio of the work ($-\mathcal{W}$) to any of Q_H and Q_L . For example, the main figure-of-merit of a thermal machine used as a heat engine ($Q_H > 0$, $Q_L > 0$, $-\mathcal{W} = |\mathcal{W}| > 0$), is its *efficiency*

$$\eta \equiv \frac{|\mathcal{W}|}{Q_H} = \frac{Q_H - Q_L}{Q_H} \equiv 1 - \frac{Q_L}{Q_H} \leq 1. \quad (1.67)$$

Heat engine's efficiency: definition

For the Carnot cycle, this definition, together with Eq. (66), immediately yields the famous relation

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}, \quad (1.68)$$

Carnot cycle's efficiency

which shows that at a given T_L (that is typically the ambient temperature ~ 300 K), the efficiency may be increased, ultimately to 1, by raising the temperature T_H of the heat source.⁴²

The unique nature of the Carnot cycle (see Fig. 9b again) makes its efficiency (68) the upper limit for any heat engine.⁴³ Indeed, in this cycle, the transfer of heat between any heat bath and the working gas is performed reversibly, when their temperatures are equal. (If this is not so, some heat may flow from the hotter to the colder bath without performing any work.) In particular, it shows that $\eta_{\text{max}} = 0$ at $T_H = T_L$, i.e., no heat engine can perform mechanical work in the absence of temperature gradients.⁴⁴

On the other hand, if the cycle is reversed (see the dashed arrows in Figs. 8 and 9), the same thermal machine may serve as a *refrigerator*, providing heat removal from the low-temperature bath ($Q_L < 0$) at the cost of consuming external mechanical work: $\mathcal{W} > 0$. This reversal does not affect the basic relation (63), which now may be used to calculate the relevant figure-of-merit, called the *cooling coefficient of performance* ($\text{COP}_{\text{cooling}}$):

$$\text{COP}_{\text{cooling}} \equiv \frac{|Q_L|}{\mathcal{W}} = \frac{Q_L}{Q_H - Q_L}. \quad (1.69)$$

Notice that this coefficient may be above unity; in particular, for the Carnot cycle we may use Eq. (66) (which is also unaffected by the cycle reversal) to get

$$(\text{COP}_{\text{cooling}})_{\text{Carnot}} = \frac{T_L}{T_H - T_L}, \quad (1.70)$$

so this value is larger than unity at $T_H < 2T_L$ and may be even *much* larger than 1 when the temperature difference ($T_H - T_L$), sustained by the refrigerator, tends to zero. For example, in a typical air-conditioning system, this difference is of the order of 10 K, while $T_L \sim 300$ K, so $(T_H - T_L) \sim T_L/30$, i.e.

⁴² Semi-quantitatively, this trend is valid also for other, less efficient but more practicable heat engine cycles – see Problems 15-18. This trend is the leading reason why internal combustion engines, with T_H of the order of 1,500 K, are more efficient than steam engines, with T_H of at most a few hundred K.

⁴³ In some alternative axiomatic systems of thermodynamics, this fact is postulated and serves the role of the 2nd law. This is why it is under persisting (predominantly, theoretical) attacks by suggestions of more efficient heat engines – notably, with quantum systems. To the best of my knowledge, reliable analyses of all the suggestions put forward so far have confirmed that the Carnot efficiency (68) cannot be exceeded even using quantum-mechanical cycles – see, e.g., the recent review by S. Bhattacharjee and A. Dutta, *Eur. J. Phys.* **94**, 239 (2021).

⁴⁴ Such a hypothetical heat engine that would violate the 2nd law of thermodynamics, is called the “perpetual motion machine of the 2nd kind” – in contrast to any (also hypothetical) “perpetual motion machine of the 1st kind” that would violate the 1st law, i.e., the energy conservation.

the Carnot value of $\text{COP}_{\text{cooling}}$ may be as high as ~ 30 . (In the state-of-the-art commercial HVAC systems it is within the range of 3 to 4.) This is why the term “cooling efficiency”, used in some textbooks instead of $(\text{COP})_{\text{cooling}}$, may be misleading.

Since in the reversed cycle $Q_H = -\mathcal{W} + Q_L < 0$, i.e. the system provides heat flow into the high-temperature heat bath, it may be used as a *heat pump* for heating purposes. The figure-of-merit appropriate for this application is different from Eq. (69):

$$\text{COP}_{\text{heating}} \equiv \frac{|Q_H|}{\mathcal{W}} = \frac{Q_H}{Q_H - Q_L}, \quad (1.71)$$

so for the Carnot cycle, using Eq. (66) again, we get

$$(\text{COP}_{\text{heating}})_{\text{Carnot}} = \frac{T_H}{T_H - T_L}. \quad (1.72)$$

Note that this COP is *always* larger than 1, meaning that the Carnot heat pump is always more efficient than the direct conversion of work into heat (when $Q_H = -\mathcal{W}$, so $\text{COP}_{\text{heating}} = 1$), though practical electricity-driven heat pumps are substantially more complex and hence more expensive than simple electric heaters. Such heat pumps, with typical $\text{COP}_{\text{heating}}$ values of around 4 in summer and 2 in winter, are frequently used for heating large buildings.

Finally, note that according to Eq. (70), the $\text{COP}_{\text{cooling}}$ of the Carnot cycle tends to zero at $T_L \rightarrow 0$, making it impossible to reach the absolute zero of temperature, and hence illustrating the meaningful (Nernst’s) formulation of the 3rd law of thermodynamics, cited in Sec. 3. Indeed, let us prescribe a finite but very large heat capacity $C(T)$ to the low-temperature bath, and use the definition of this variable to write the following expression for the relatively small change of its temperature as a result of dn similar refrigeration cycles:

$$C(T_L)dT_L = Q_L dn. \quad (1.73)$$

Together with Eq. (66), this relation yields

$$\frac{C(T_L)dT_L}{T_L} = -\frac{|Q_H|}{T_H} dn. \quad (1.74)$$

If $T_L \rightarrow 0$, so $T_H \gg T_L$ and $|Q_H| \approx -\mathcal{W} = \text{const}$, the right-hand side of this equation does not depend on T_L , so if we integrate it over many ($n \gg 1$) cycles, getting the following simple relation between the initial and final values of T_L :

$$\int_{T_{\text{ini}}}^{T_{\text{fin}}} \frac{C(T)dT}{T} = -\frac{|Q_H|}{T_H} n. \quad (1.75)$$

For example, if $C(T)$ is a constant, Eq. (75) yields an exponential law,

$$T_{\text{fin}} = T_{\text{ini}} \exp\left\{-\frac{|Q_H|}{CT_H} n\right\}, \quad (1.76)$$

with the absolute zero of temperature not reached as any finite n . Even for an arbitrary function $C(T)$ that does not vanish at $T \rightarrow 0$, Eq. (74) proves the Nernst theorem, because dn diverges at $T_L \rightarrow 0$.

1.7. Exercise problems

1.1. Two bodies, with temperature-independent heat capacities $C_{1,2}$ and initial temperatures $T_{1,2}$ are placed into a weak thermal contact. Calculate the change of the total entropy of the system before it reaches thermal equilibrium.

1.2. A gas portion has the following properties:

- (i) its heat capacity $C_V = aT^b$, and
- (ii) the work \mathcal{W}_T needed for its isothermal compression from V_2 to V_1 equals $cT\ln(V_2/V_1)$,

where a , b , and c are some constants. Find the equation of state of the gas and calculate the temperature dependences of its entropy S and thermodynamic potentials E , H , F , G , and Ω .

1.3. A volume with an ideal classical gas of similar molecules is separated into two parts with a partition so that the number N of molecules in each part is the same but their volumes are different. The gas is initially in thermal equilibrium with the environment, and its pressure in one part is P_1 , and in the other part, P_2 . Calculate the change of entropy resulting from a fast removal of the partition.

1.4. An ideal classical gas of N particles is initially confined to volume V , and is in thermal equilibrium with a heat bath of temperature T . Then the gas is allowed to expand to volume $V' > V$ in one of the following ways:

- (i) The expansion is slow, so due to the sustained thermal contact with the heat bath, the gas temperature remains equal to T .
- (ii) The partition separating the volumes V and $(V' - V)$ is removed very fast, allowing the gas to expand rapidly.

For each case, calculate the changes of pressure, temperature, energy, and entropy of the gas during its expansion, and compare the results.

1.5. For an ideal classical gas with temperature-independent specific heat, derive the relation between P and V at its adiabatic expansion/compression.

1.6. Calculate the speed and the wave impedance of acoustic waves propagating in an ideal classical gas with temperature-independent specific heat, in the limits when the propagation may be treated as:

- (i) an isothermal process, and
- (ii) an adiabatic process.

Which of these limits is achieved at higher wave frequencies?

1.7. As will be discussed in Sec. 3.5, the so-called “hardball” models of classical particle interaction yield the following equation of state of a gas of such particles:

$$P = T\varphi(n),$$

where $n = N/V$ is the particle density, while the function $\varphi(n)$ is generally different from that ($\varphi_{\text{ideal}}(n) = n$) of the ideal gas but still independent of temperature. For such a gas, with a temperature-independent c_V , calculate:

- (i) the energy of the gas, and
(ii) its pressure as a function of n at an adiabatic compression.

1.8. For an arbitrary thermodynamic system with a fixed number of particles, prove the four *Maxwell relations* (already mentioned in Sec. 4):

$$\begin{aligned} \text{(i): } \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V, & \text{(ii): } \left(\frac{\partial V}{\partial S}\right)_P &= \left(\frac{\partial T}{\partial P}\right)_S, \\ \text{(iii): } \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P, & \text{(iv): } \left(\frac{\partial P}{\partial S}\right)_V &= -\left(\frac{\partial T}{\partial V}\right)_S, \end{aligned}$$

and also the following formula:

$$\text{(v): } \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

1.9. Express the difference ($C_P - C_V$) between the heat capacities of a system via its equation of state $P = P(V, T)$.

1.10. Prove that the *isothermal compressibility*⁴⁵ of a system of N similar particles,

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

may be expressed in two different ways:

$$\kappa_T = \frac{V^2}{N^2}\left(\frac{\partial^2 P}{\partial \mu^2}\right)_T = \frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

1.11 *Throttling*⁴⁶ is an expansion of gas by driving it through either a small hole (called the *throttling valve*) or a porous partition, using an externally sustained difference of pressure values on two sides of such an obstacle.

(i) Prove that in the absence of heat exchange with the environment, the enthalpy of the transferred gas does not change.

(ii) Express the *Joule-Thomson coefficient* $(\partial T/\partial P)_H$, which characterizes the gas temperature change at throttling, via its thermal expansion coefficient $\alpha \equiv (\partial V/\partial T)_P/V$.

1.12. A system with a fixed number of particles is in thermal and mechanical contact with its environment of temperature T_0 and pressure P_0 . Assuming that the internal relaxation of the system is sufficiently fast, derive the conditions of stability of its equilibrium with the environment with respect to small perturbations.

1.13. Derive the analog of the relation for the difference ($C_P - C_V$), whose derivation was the task of Problem 9, for a fixed-volume sample with a uniform magnetization \mathcal{M} parallel to the uniform

⁴⁵ Note that the compressibility is just the reciprocal bulk modulus, $\kappa = 1/K$ – see, e.g., CM Sec. 7.3.

⁴⁶ Sometimes it is called the *Joule-Thomson process*, though more typically, the latter term refers to the possible gas cooling at the throttling.

external field \mathcal{H} . Spell out this result for a paramagnet that obeys the *Curie law* $\mathcal{M} \propto \mathcal{H}T$ – the relation to be derived and discussed later in this course.

1.14. Two bodies have equal temperature-independent heat capacities C but different temperatures, $T_1 > T_2$. Calculate the maximum mechanical work obtainable from this system by using a heat engine.

1.15. Express the efficiency η of a heat engine that uses the so-called *Joule* (or “Brayton”) cycle consisting of two adiabatic and two isobaric processes (see the figure on the right), via the highest and lowest values of pressure, and compare the result with η_{Carnot} . Assume an ideal classical working gas with temperature-independent C_P and C_V .

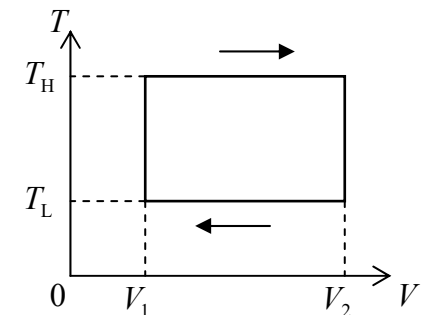
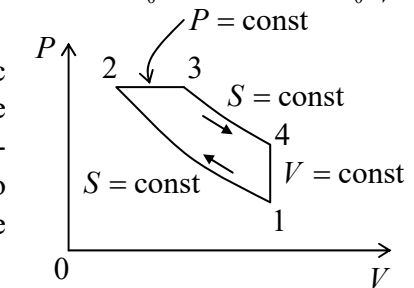
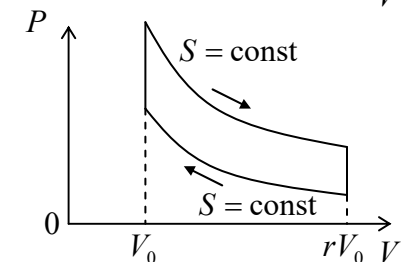
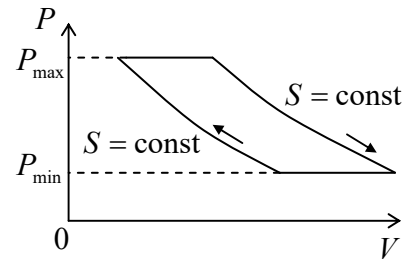
1.16. Calculate the efficiency of a heat engine using the *Otto cycle*⁴⁷ that consists of two adiabatic and two isochoric (constant-volume) reversible processes – see the figure on the right. Explore how the efficiency depends on the *compression ratio* $r \equiv V_{\text{max}}/V_{\text{min}}$, and compare it with the Carnot cycle’s efficiency. Assume an ideal classical working gas with temperature-independent heat capacity.

1.17. The *Diesel cycle* (an approximate model of the Diesel internal combustion engine’s operation) consists of two adiabatic processes, one isochoric process, and one isobaric process – see the figure on the right. Assuming an ideal working gas with temperature-independent C_V and C_P , express the cycle’s efficiency η via its two dimensionless parameters: the so-called *cutoff ratio* $\alpha \equiv V_3/V_2 > 1$ and the compression ratio $r \equiv V_1/V_2 > \alpha$.

1.18. A heat engine’s cycle consists of two isothermal ($T = \text{const}$) and two isochoric ($V = \text{const}$) processes – see the figure on the right.⁴⁸

(i) Assuming that the working gas is an ideal classical gas of N particles, calculate the mechanical work performed by the engine during one cycle.

(ii) Are the specified conditions sufficient to calculate the engine’s efficiency? (Justify your answer.)



⁴⁷ This name stems from the fact that the cycle is an approximate model of operation of the four-stroke internal combustion (“petrol”) engine, which was improved and made practicable by N. Otto in 1876 – though its idea had been conceived earlier (in 1860) by É. Lenoir.

⁴⁸ The reversed cycle of this type is a reasonable approximation for the operation of the *Stirling* and *Gifford-McMahon* (GM) refrigerators, broadly used for *cryocooling* – for a recent review, see, e.g., A. de Waele, *J. Low Temp. Phys.* **164**, 179 (2011).