Chapter 10
Elements of Equilibrium Statistical Thermodynamics

During the development of phenomenological thermodynamics, several scientists tried to interpret its formalism on the basis of the movement of the multitude of molecules contained in the system. The first success of this effort was the derivation of equations of state of gases, which has inspired the name *kinetic theory of gases* for these calculations. Despite this success, the theory contained several contradictions, which could not be solved. (An important shortcoming was the fact that the description based on classical mechanics was symmetrical to the inversion of time, while real thermodynamic phenomena are irreversible with respect to time.) The breakthrough was made by Maxwell and Boltzmann who made use of the *probability distribution* of the energy of molecules. This invention led Boltzmann to the molecular interpretation of the second law of thermodynamics, thus explaining also the nature of entropy. In the last few years of the nineteenth century, Gibbs generalized and systematized the theory founded by Maxwell and Boltzmann to interpret thermodynamics on a statistical basis, and he also coined the expression *statistical mechanics*. In the first two decades of the twentieth century, the development of quantum mechanics enabled the understanding of the underlying physical basis of the formalism of statistical mechanics.

As it is stated in this book prior to the discussion of the postulates of thermodynamics, the number of particles in a macroscopic quantity of material is of the order of magnitude of the Avogadro constant (6.022×10^{23} particles/mol), thus it is hopeless to describe the behavior of individual particles; we must be satisfied with the description of the mean behavior of their assembly. Having realized this, it is immediately obvious that we should describe the large ensemble of molecules by the methods of probability theory. When comparing quantities calculated using probability theory with macroscopic observations, some mean properties of the assembly of particles – that is, *expected values* – can be identified with thermodynamic quantities. There are a surprisingly low number of such properties; thus, this description of the system leads to results readily applicable in thermodynamics. The foundation of thermodynamics based on this approach is called *statistical thermodynamics*, or, in a more general sense, *statistical physics*. Using this approach, equilibrium thermodynamics can be constructed in a simpler way, using fewer

E. Keszei, *Chemical Thermodynamics*,
DOI 10.1007/978-3-642-19864-9_10,

postulates than in the phenomenological theory. However, we shall not follow the way of complete deduction of thermodynamics from the principles of statistical physics, as we have already introduced thermodynamics in a phenomenological postulatory manner. Instead, we suppose prior knowledge of thermodynamic principles and quantities and deal only with actual *calculations* of thermodynamic properties. As we shall see, this approach can lead to the calculation of the fundamental equations in a multitude of systems based on molecular properties of the constituent particles.

From the basic quantities used in thermodynamics, most of them – for example, the (internal) energy U, the composition n_i, the pressure P, the volume V – were already known from mechanics and chemistry, except for the entropy S and the temperature T. However, temperature was a quantity that could be measured even prior to thermodynamic theory; contrary to the entropy, which is derived from other measurable quantities using thermodynamic formalism. Therefore, one of the main thrusts of statistical thermodynamics is to determine entropy based on the mechanical behavior of the multitude of particles. Once the entropy of a system is determined as a function of U, V and the composition data n_i, it is a fundamental equation,[1] which enables to calculate any thermodynamic properties in any states (cf. Sect. 4.4.3).

10.1 The Microcanonical Ensemble

The foundations of phenomenological thermodynamics were developed first for simple, isolated systems. For similar reasons, we begin the treatment of statistical thermodynamics for the same systems, adding a further simplification of restricting the treatment to a *single component*. The *mechanical model* of a simple, isolated single-component system is a population of N identical molecules placed in a fixed volume V, having a fixed overall energy E. Following Gibbs, we call this model a *microcanonical ensemble*,[2] though it is also called as an N, V, E ensemble. Note that the composition variable is not the usual amount of substance n but the number of molecules N; as we describe molecular properties. The relation between the two variables is provided by the Avogadro constant N_A.

The microcanonical ensemble can be interpreted in two ways. It can be thought of as a real ensemble consisting of a very large number of isolated systems in *different states* in accordance with the fixed values of N, V, and E. As these states are not discernable macroscopically, they are called *microstates*. It can also be thought of as a temporal succession of microstates in the same isolated system, where the microstate of the system changes in time but conserves the same values of

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[1] This is of course only true if we deal with *simple systems*, where the system cannot change energy with the surroundings but by means of volume work and heat. For more complicated systems, we have to include other extensive variables characterizing additional interactions.

[2] The origin of the name is related to the *canonical ensemble*. (See according footnote.)

N, V, and E. According to the *ergodic hypothesis*,[3] the expected values of thermodynamic interest of a random variable over time and that over the ensemble are the same. Consequently, from a statistical point of view, the only relevant information is the probability of individual microstates of the ensemble, which is given by the probability distribution function over the microstates.

It is important to specify what does the notion "state" means from a statistical point of view. A state – as it refers to a large assembly of molecules – is to be understood in a quantum mechanical sense, that is, those states are considered to be different, which differ at least in one quantum number. However, quantum states of a *macroscopic* system are quite different from what we have learnt for individual isolated molecules. The number of different states for the multitude of molecules having complicated interactions is in the order of the magnitude of the Avogadro constant. As the energy of the system is finite, the energy of "neighboring" microstates is only slightly different. As a consequence, the system can have rather easy transitions between such states. (This can happen, for example, in case of collisions of the particles when they can exchange some energy – while the overall energy of the system remains unchanged.) According to quantum mechanics, such "easy" transitions can also happen by random fluctuations. From the point of view of the distribution of states, it means that each state has an equal probability. This principle is expressed by the *only postulate* of (equilibrium) statistical thermodynamics:

In a microcanonical ensemble, every permissible quantum state conform to the conditions of fixed N, E and V occurs with equal probability if the ensemble represents the equilibrium state of the system.

Let us discuss the consequences of this postulate. A particle system with a macroscopic constraint in a given quantum state quickly undergoes transitions exploring many microstates. As the probability of these microstates is equal, the system explores *all states* within finite time, thus attaining equilibrium. Removing the constraint (e.g., removing an internal wall) opens up the possibility of previously precluded microstates. As the system experiences again that the entirety of the states (now including new states) is equally probable, it will explore the newly available microstates as well within a finite time while attaining the new equilibrium. This means that the system explores the *maximum* of the permitted states available in equilibrium. This maximum principle reminds us of Postulate 2 of thermodynamics – what we shall consider more thoroughly later.

Another interesting point is the behavior of the system starting from a particular microstate, after a few transitions, if we suddenly reverse the time axis. In a mechanical system, movements are symmetrical with respect to the inversion of time, thus the system should go back to the starting microstate after exactly the same number of transitions as it took to reach the state of inversion. Now, the postulate formulated above makes this return impossible; the transition being *equally probable to any state* makes the system to explore them in a random way,

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[3] The word ergodic has been coined by Boltzmann from the Greek words $\varepsilon\rho\gamma o\nu =$ work and ʽ$o\delta o\varsigma =$ path.

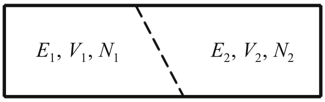

Fig. 10.1 A microcanonical ensemble divided into two parts, which corresponds to an isolated system divided into two subsystems

thus necessarily losing the way back to where it came from. Consequently, the postulate assures the irreversibility of thermodynamic processes.

Let us discuss the consequences of the maximum principle mentioned above. Consider a thermodynamic system modeled by an E, V, N ensemble virtually divided into two parts, using the notation of Fig. 10.1.

As the variables of the entropy function $S(E, V, N)$ are extensive, the following equations hold:

$$\begin{aligned} N &= N_1 + N_2, \\ V &= V_1 + V_2, \\ E &= E_1 + E_2. \end{aligned} \tag{10.1}$$

Entropy is an extensive quantity, thus we can write the additivity relation:

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2). \tag{10.2}$$

It is easy to recognize that the number of states in the entire system is the *product* of the number of states in the two subsystems. (As to each individual state in one of the subsystems, we can have any one of the other subsystem.) Denoting the number of states by the capital Greek letter Ω, we can write this property as:

$$\Omega(E, V, N) = \Omega_1(E_1, V_1, N_1)\ \Omega_2(E_2, V_2, N_2). \tag{10.3}$$

Taking the logarithm of both sides, the equation still holds:

$$\ln\Omega(E, V, N) = \ln\ \Omega_1(E_1, V_1, N_1) + \ln\ \Omega_2(E_2, V_2, N_2). \tag{10.4}$$

Comparing this with the additivity relation of entropy, we can conclude that the function $S(E, V, N)$ differs only by a constant factor from the function $\Omega(E, V, N)$:

$$S(E, V, N) = k\ln\ \Omega(E, V, N). \tag{10.5}$$

This is the expression of *entropy as a function of the number of states* in a microcanonical ensemble. The function $\Omega(E, V, N)$ is called the *microcanonical partition function*. Thus, we can state that we have reached the goal of statistical considerations; by determining the possible number Ω of microstates as a function of E, V and N and multiplying its logarithm by k, we get the entropy-based fundamental equation.[4] The partition function also specifies the probability distribution function over the microstates. All the Ω states are equally probable, thus this function is a constant for all microstates i:

$$p_i = \frac{1}{\Omega}. \tag{10.6}$$

(The sum of the probabilities of all possible states should give unit.)

The constant k should be chosen so that the scale of entropy is identical to that used in phenomenological thermodynamics. Obviously, the zero point of the scale is independent of the choice of k, as the possible minimum of the number of states is 1. We get the well-known entropy scale by choosing the constant as R/N_A, the gas constant divided by the Avogadro constant. It is "the gas constant for a single particle", $k = 1.3807 \times 10^{-23}$ J/K, and it is called the *Boltzmann constant*. This choice also guarantees that the partial derivative of the function $S(E, V, N)$ is exactly the inverse of temperature, $1/T$, in K units.

10.1.1 Statistical Thermodynamics of the Einstein Solid in Microcanonical Representation

Let us discuss an early example of statistical entropy calculations, the Einstein model of a crystalline solid. In this model, identical particles are localized in each position of the crystal lattice, which are considered as three-dimensional harmonic oscillators with the same ground state frequency ω_0 in the three directions. (This is identical to the assumption that the attractive forces pulling the particle back to the lattice point are proportional to the deflection and are the same in each direction.) The model does not consider different states of the nuclei or electrons but the excitation of the lattice vibrations. The N lattice points are coupled together, thus the entire crystal can have $3N$ collective vibrational modes. The lowest possible frequency is very close to zero (equivalent to a wavelength that fits into the macroscopic crystal), while the highest permissible frequency corresponds to a wavelength comparable to the interparticle distance in the crystal. Following Einstein, this can be modeled by distributing the internal energy U among the $3N$ harmonic oscillators. Each oscillator can have a frequency which is a multiple integer of ω_0. The energy of a harmonic oscillator is given by,

$$E = \hbar\omega_0\left(n + \frac{1}{2}\right), \tag{10.7}$$

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[4] Boltzmann used the name "thermodynamic *probability*" (*Wahrscheinlichkeit* in German) for the number of states whence the notation W originally used by him. This has been changed in English to a Greek letter of similar shape and role ω, which in turn got capitalized to become Ω.

where $\hbar = h/2\pi = 1.055 \times 10^{-34}$ Js is *Planck's constant*. Fixing the zero level of energy at $\hbar\omega_0/2$, the energy of the oscillator can assume the discrete values that are multiples of $\hbar\omega_0$ (one vibrational energy quantum), including zero.

The physical model can be "translated" into mathematical language the following way. The internal energy U is available in the form of $U/\hbar\omega_0$ vibrational quanta that can be distributed among the $3N$ oscillators. What is the number of possible states that corresponds to this condition? An equivalent problem is to distribute $U/\hbar\omega_0$ pebbles in $3N$ (distinguishable) boxes. (Lattice points are distinguishable as they are fixed to one single position in the crystal.) This is a simple combinatorial task, but it can be further simplified – as shown in Fig.10.2.

At the bottom of the figure, we can see the beginning and the end of a possible arrangement of $U/\hbar\omega_0$ indistinguishable pebbles and $3N - 1$ indistinguishable bars in a row. The number of possible arrangements is exactly the same as in case of the original distribution of pebbles in boxes as shown at the top of the figure. Using combinatorial terms, this is the number of permutation of $U/\hbar\omega_0 + 3N - 1$ elements with repetition, where there are $U/\hbar\omega_0$ identical elements of the first kind (pebbles) and $3N - 1$ identical elements of the second kind (bars). From combinatorial identities, we can write this number as:

$$\Omega = P^{\frac{U}{\hbar\omega_0},3N-1}_{\frac{U}{\hbar\omega_0}+3N-1} = \frac{\left(3N - 1 + \frac{U}{\hbar\omega_0}\right)!}{(3N-1)!\left(\frac{U}{\hbar\omega_0}\right)!}. \tag{10.8}$$

We can simplify the notation by introducing $a = 3N - 1$ and $b = U/\hbar\omega_0$, thus the calculation of Ω is equivalent to the calculation of $\frac{(a+b)!}{a!b!}$. As the number of lattice points N is rather large (it is in the order of magnitude of 10^{23}), we can use the Stirling formula to calculate the factorial, which is valid to a good approximation if $N \gg 1$:

$$\ln(N!) = N \ln N - N. \tag{10.9}$$

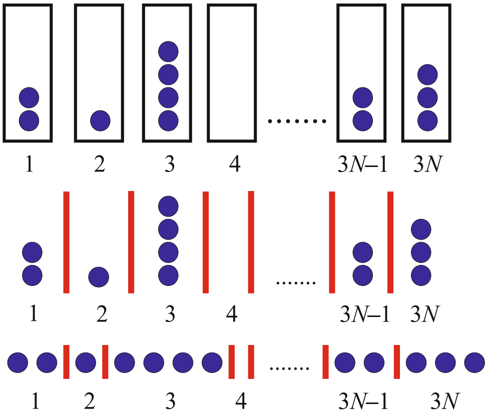

Fig. 10.2 Three equivalent formal models of the Einstein solid. *First row*: distribution of $U/\hbar\omega_0$ pebbles in $3N$ distinguishable boxes. *Second row*: division of $U/\hbar\omega_0$ indistinguishable pebbles into stacks using $3N - 1$ bars. *Third row*: arrangement of $U/\hbar\omega_0$ indistinguishable pebbles and $3N - 1$ indistinguishable bars in a row

This formula provides the logarithm of the factorial, which readily leads to ln Ω. Starting with the calculation of the simplified notation, we get:

$$\begin{aligned}\ln\frac{(a+b)!}{a!b!} &= \ln(a+b)! - \ln a! - \ln b! \cong (a+b)\ln(a+b) - a\ln a - b\ln b = \\ & a[\ln(a+b) - \ln a] - b[\ln(a+b) - \ln b] = a\ln\frac{a+b}{a} + b\ln\frac{a+b}{b} \\ &= a\ln\left(1+\frac{b}{a}\right) + b\ln\left(1+\frac{a}{b}\right).\end{aligned} \tag{10.10}$$

Resubstituting a and b, the entropy function can be written as follows:

$$S = 3kN\ln\left(1+\frac{U}{3N\hbar\omega_0}\right) + \frac{kU}{\hbar\omega_0}\ln\left(1+\frac{3N\hbar\omega_0}{U}\right). \tag{10.11}$$

Rewriting this N-particle formula for particles of Avogadro-number, we get the (intensive) molar entropy s:

$$s = 3kN_\mathrm{A}\ln\left(1+\frac{u}{3N_\mathrm{A}\hbar\omega_0}\right) + \frac{3N_\mathrm{A}ku}{3N_\mathrm{A}\hbar\omega_0}\ln\left(1+\frac{3N_\mathrm{A}\hbar\omega_0}{u}\right), \tag{10.12}$$

with u being the molar internal energy. Let us substitute R in place of kN_A and u_0 in place of $3N_\mathrm{A}\hbar\omega_0$ (i.e., the reference state is the one when every oscillator has an average energy $\hbar\omega_0$). Thus, the molar entropy becomes

$$s = 3R\ln\left(1+\frac{u}{u_0}\right) + 3R\frac{u}{u_0}\ln\left(1+\frac{u_0}{u}\right), \tag{10.13}$$

which is a compact form of the fundamental equation of the Einstein solid. Note that this is an *intensive* equation of state, thus it does not contain N as a variable.

Partial derivation of this entropy function with respect to u leads to the inverse temperature. From the function $1/T$, we can express u as a function of temperature. Derivating the u function with respect to T provides the molar heat capacity c_V. Without showing the details of these calculations, we mention that the value of the c_V function thus obtained is zero at $T = 0$ and rises exponentially with temperature until saturation, when it becomes a constant. This constant is identical for many solids with the experimentally determined heat capacity. This tendency is also in accordance with the experiments, thus the thermal properties of the Einstein solid qualitatively reflect the behavior of crystals. However, this is not the case for the mechanical properties; as it can be seen from (10.13), the calculated entropy *does not depend* on volume. Accordingly, the pressure we can calculate as $P = T\left(\frac{ds}{dv}\right)_u$

[see e.g., (2.53)] is zero, which is evidently a contradiction. Thus, the Einstein model of solids cannot be used even qualitatively for mechanical purposes.[5]

10.1.2 Statistical Thermodynamics of a System of Two-State Molecules in Microcanonical Representation

Another example that illustrates the usefulness of statistical thermodynamics in calculating the entropy is a system of a single component consisting of molecules that have a ground state (which is the zero level of energy) and an excited state having a molecular energy ε. There exist similar molecules in reality as well, having two relatively low energy levels, their third and higher energy states having much higher energies so that they are not populated at moderate temperatures. In the corresponding microcanonical ensemble, there are U/ε molecules in the excited state and $N - U/\varepsilon$ molecules in the ground state.

The number of possible states can be calculated using combinatorial considerations. The task is now to determine the number of ways of choosing U/ε molecules out of the N molecules, which is the number of combinations without repetition of U/ε elements chosen from the total number of N elements:

$$\Omega = C_{N,\frac{U}{\varepsilon}} = \frac{N!}{\frac{U}{\varepsilon}!\left(N - \frac{U}{\varepsilon}\right)!}. \tag{10.14}$$

Let us simplify the notation again by introducing $a = N$ and $b = U/\varepsilon$, thus the calculation of Ω is equivalent to the calculation of $\frac{a!}{b!(a-b)!}$. Let us apply again the Stirling formula for large numbers to approximate the logarithm of their factorial:

$$\ln \frac{a!}{b!(a-b)!} = a \ln a - b \ln b - (a - b) \ln(a - b). \tag{10.15}$$

After some rearrangement and addition of the terms $-b \ln a + b \ln a$ resulting in zero, we get:

$$\begin{aligned}&(b - a) \ln(a - b) - b \ln b + a \ln a - b \ln a + b \ln a\\ &\quad = (b - a) \ln \frac{a - b}{a} - b \ln \frac{b}{a}.\end{aligned} \tag{10.16}$$

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[5] Despite this inadequacy, the Einstein solid played an important role in the history of thermodynamics. The experimental evidence already known for a long time that the molar heat capacity of solids changes with temperature could not be explained before. It was Einstein who succeeded to give this explanation by using the results of both quantum mechanics and statistical physics.

Resubstituting N and U/ε, we obtain the expression of entropy:

$$S = k \ln \Omega = \left(\frac{U}{\varepsilon} - N\right) k \ln\left(1 - \frac{U}{N\varepsilon}\right) - \frac{U}{\varepsilon} k \ln \frac{U}{N\varepsilon}. \tag{10.17}$$

Obviously, this entropy function is also independent of volume, thus its mechanical properties are not satisfactory. However, the thermal properties are correct; for example, temperature is always positive, what we can check as follows:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} = \frac{k}{\varepsilon} \ln\left(\frac{N\varepsilon}{U} - 1\right). \tag{10.18}$$

Solving this equation of state for the internal energy U, we get the energy function:

$$U = \frac{N\varepsilon}{1 + e^{\frac{\varepsilon}{kT}}}. \tag{10.19}$$

Obviously, the limit of the exponential when $T \to \infty$ is unit, and that of the energy is $N\varepsilon/2$. Accordingly, $U \le (N\varepsilon/2)$, thus the inverse temperature given by (10.18) is nonnegative, which means that the temperature may be positive or zero. It also follows from the result that at very high temperatures, half of the molecules *were* in the excited state – if higher excited states were not occupied.

Let us write the Avogadro number N_A in the above function to get the *molar internal energy*. By deriving it with respect to T, we get the molar heat capacity:

$$c_V = \left(\frac{\partial u}{\partial T}\right)_{V,N} = N_A \varepsilon \frac{-1}{\left(e^{\frac{\varepsilon}{kT}} + 1\right)^2} e^{\frac{\varepsilon}{kT}} \frac{\varepsilon}{k}\left(-\frac{1}{T^2}\right) = \ln\left(\frac{N_A \varepsilon}{U} - 1\right). \tag{10.20}$$

Resubstituting U and rearranging we obtain

$$c_V = \frac{N_A \varepsilon^2}{kT^2} \frac{e^{\frac{\varepsilon}{kT}}}{\left(e^{\frac{\varepsilon}{kT}} + 1\right)^2}. \tag{10.21}$$

Experimental data support that, if the heat capacity function c_V is of the shape predicted by the above equation (see Fig. 10.3), molecules have two low-lying energy levels, and their higher excited states have much higher energy.

It was not only for demonstrative purposes that we discussed such relatively simple systems; in a typical real-life case, combinatorial analogies lead to problems too much difficult where Ω cannot be calculated. There is another possibility to calculate Ω; the calculation by integrals of points on an isoenergetical surface in multidimensional space modeling the microcanonical systems. However, the integrals thus emerging cannot be calculated in more complicated cases either.

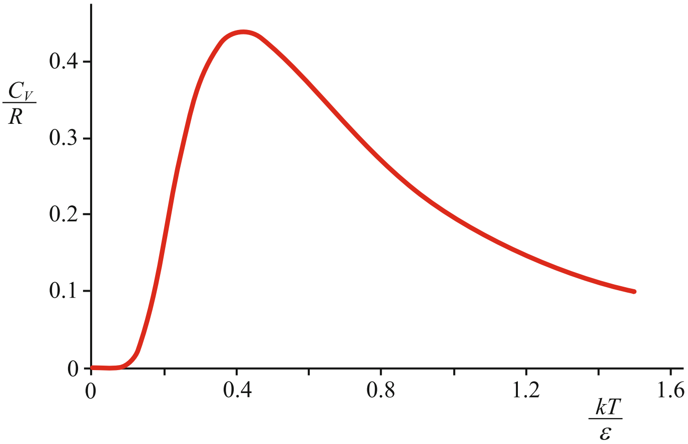

Fig. 10.3 Molar heat capacity c_V in units of R as a function of temperature in units of k/ε for a system of two-state molecules

This is the reason to calculate other entropy-like functions instead of entropy itself, over different ensembles than the microcanonical one. As an example, we shall discuss the *canonical ensemble* in the next section.

10.2 The Canonical Ensemble

The (single component) *canonical ensemble*[6] is the mechanical model of a simple thermodynamic system which is closed, has rigid diathermal walls, and is immersed in a heat reservoir of constant temperature. The reservoir behaves as a thermostat, keeping the temperature of the system constant even if heat would be absorbed or released inside the system. Thus, the canonical ensemble – also called as an N, V, T ensemble – consists of N particles enclosed in a constant volume V, having a constant temperature T. Note that it can have *any energy* which is consistent with these conditions. Accordingly, the elements of the ensemble are replicates of N particles in a fixed volume V that have different energies. (We can also say that the canonical ensemble consists of microcanonical ensembles as elements having the same volume V and particle number N but different energy.) The canonical ensemble can also be considered as a temporal succession of its elements; it is the manifold of particles consistent with the condition of constant N, V, and T, but its successive states – as a consequence of energy exchange with the thermostat – have

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[6] The word *canonical* originates from the Greek noun $\kappa\alpha\nu\omega\nu$ (measuring rod; in a figurative sense: rule) via the Latin noun *canon* = rule, whence the Latin adjective *canonicus* = regular. The name *canonical ensemble* was coined by Gibbs, who obviously considered the N, V, T ensemble as "regular" and the N, V, E ensemble as "little regular". This latter name is an allusion to the property that microcanonical ensembles are included in a canonical ensemble.

a constantly changing energy. The ergodic hypothesis is valid also for this ensemble; the expected values of a random variable of thermodynamic interest over time and that over the ensemble are the same.

Considering the reservoir (including the closed, constant-volume, and constant-temperature inner subsystem) as an isolated system having constant volume, energy and particle number, it can be modeled as a microcanonical ensemble. By doing so, we can reduce the characterization of the canonical ensemble to that of the already known microcanonical ensemble. The most important difference between the microcanonical and canonical ensemble is that the probability of each state is identical in the former, which is no more true in the latter; the probabilities of different states are different. Using combinatorial methods based on the uniform distribution of states inside the reservoir, we can derive the probability distribution over the states in the canonical ensemble included. However, we shall discuss a simple analogy first to illustrate this kind of calculation, and then we will generalize the result for a canonical ensemble.

Let us consider the example of three dice, one of them black and the other two white. The set of two white dice is the analog of the reservoir, the black one corresponds to the "thermostated" system inside. The fixed energy of the entire system containing both reservoir and the constant-temperature subsystem corresponds to a fixed sum when throwing the three dice. We have to determine the conditional probability of the values on the black die provided that the sum on the three dice is always the prescribed value. Let us choose this value to be 12. Table 10.1 summarizes the possible outcomes that fulfill this constraint. The results are grouped according to the value on the black die (the "energy" of the subsystem). As the sum can only be 12 given the actual value of the black die, there are as much possibilities as listed in the second column of the table. We can read from the table that there are altogether 25 different possibilities which have equal probabilities, thus the probability of one actual set of values is 1/25. Accordingly, the conditional probability of a given number on the black die is 1/25 times the number of possibilities listed in the second column. This value is written in the column marked "probability."

The rule explored discussing the above example can be generalized as follows. The probability of the state of a subsystem is equal to the total number of the states

Table 10.1 Conditional probabilities when throwing a black and two white dice provided that the sum on the three dice is always 12

Black die	1st white/2nd white	Possibilities	Probability
1	5/6, 6/5	2	2/25
2	5/5, 4/6, 6/4	3	3/25
3	3/6, 6/3, 4/5, 5/4	4	4/25
4	4/4, 2/6, 6/2, 3/5, 5/3	5	5/25
5	1/6, 6/1, 2/5, 5/2, 3/4, 4/3	6	6/25
6	3/3, 1/5, 5/1, 2/4, 4/2	5	5/25
	Sum	25	1

of the reservoir (without the inner subsystem), compatible with the condition in the case of this particular state, divided by the number of all the possible states (of the entire system) compatible with the condition.

Let us apply this generalized rule for the case shown in Fig. 10.4, when the energy of the subsystem is E_i, and the total energy (of reservoir plus subsystem) is $E_{tot} = E_{res} + E_i$.

Let us denote the microcanonical partition function of the reservoir by Ω_{res} and that of the entire system by Ω_{tot}. The probability p_i that the energy of the inner subsystem is E_i can be calculated in the following way:

$$p_i = \frac{\Omega_{res}(E_{tot} - E_i)}{\Omega_{tot}(E_{tot})}. \tag{10.22}$$

(To simplify notation, we dropped the variables N and V, which does not depend on the index i.)

Let us substitute for Ω_{res} and Ω_{tot} their values expressed as a function of entropy, using the inverted function of (10.5):

$$p_i = \frac{e^{\frac{S_{res}(E_{tot}-E_i)}{k}}}{e^{\frac{S_{tot}(E_{tot})}{k}}} = e^{\frac{S_{res}(E_{tot}-E_i)-S_{tot}(E_{tot})}{k}}. \tag{10.23}$$

Let us denote the equilibrium energy of the inner subsystem (the expected value of energy) as usual by U. Due to the additivity of entropy, we can write:

$$S(E_{tot}) = S(U) + S_{res}(E_{tot} - U). \tag{10.24}$$

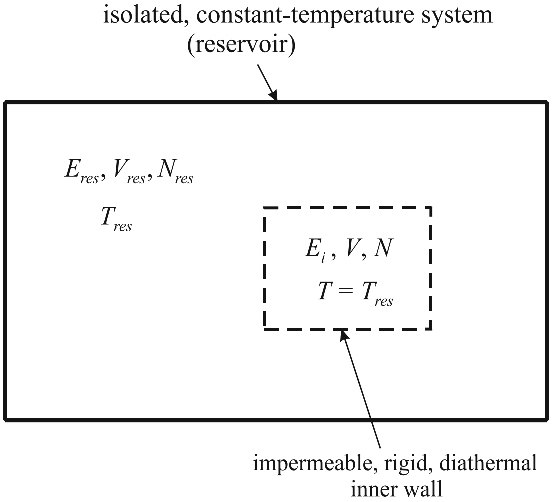

Fig. 10.4 An element of a canonical ensemble having energy E_i (*inner system*; *dashed rectangle*), and the microcanonical ensemble containing it, having a fixed energy $E_{tot} = E_{res} + E_i$ (*entire system*; *solid rectangle*). The part of the *entire system* outside the *dashed rectangle* serves as an energy reservoir having a constant temperature T_{res}, keeping the temperature of the *inner system* also constant

The entropy function $S_{res}(E_{tot} - E_i)$ can be expanded around the energy U:

$$S_{res}(E_{tot} - E_i) = S_{res}(E_{tot} - U + U - E_i) = S_{res}(U) + \frac{\partial S_{res}}{\partial U}(U - E_i) + \ldots. \tag{10.25}$$

We could write in place of .... the product of higher order derivatives of S_{res} and the appropriate powers of the difference $(U - E_i)$. However, as the expected value U differs only slightly from the actual energy E_i, the second power of $(U - E_i)$ is already negligibly small compared to $(U - E_i)$ itself, thus we can neglect higher than first-order terms in the power series. This can be easily supported by various arguments. First, we could choose an arbitrarily large reservoir ensuring that $E_{tot} \gg U$, thus $(U - E_i) \ll (E_{tot} + E_i)$ also applies. Second, we know from thermodynamics that $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$, from which it follows that the energy exchanged between the inner system and the reservoir is exactly $\frac{1}{T}\mathrm{d}U$. Truncating the power series after the first derivative and writing $\frac{1}{T}$ in place of $\left(\frac{\partial S}{\partial U}\right)_{V,N}$, we get the following equation:

$$S_{res}(E_{tot} - E_i) = S_{res}(E_{tot} - U) + \frac{U - E_i}{T}. \tag{10.26}$$

Using again the additivity of the entropy, we can write the identity:

$$S_{tot}(E_{tot}) = S(U) + S_{res}(E_{tot} - U). \tag{10.27}$$

Let us substitute the above expressions of S_{res} and S_{tot} into the exponent of the expression (10.23) of p_i:

$$S_{res}(E_{tot} - E_i) - S_{tot}(E_{tot}) = \frac{U - E_i}{T} - S(U). \tag{10.28}$$

After some rearrangement, we get the following relation:

$$\frac{U - E_i}{T} - S(U) = \frac{-E_i}{T} + \frac{U - TS(U)}{T}. \tag{10.29}$$

We can clearly see here what we could presuppose from our knowledge of phenomenological thermodynamics; there are no properties concerning either the reservoir or the entire system in this relation, only those concerning the inner system, that is, the canonical ensemble. Substituting the exponents into (10.23), we can write the probability density function we were looking for:

$$p_i = e^{-\frac{E_i}{kT}} \cdot e^{\frac{U - TS(U)}{kT}}. \tag{10.30}$$

Conform to the old habit in statistical thermodynamics, we can somewhat simplify the notation by introducing $\beta = \frac{1}{kT}$. Let us also substitute the well-known function $F = U - TS$. Thus, the probability distribution can be rewritten as:

$$p_i = e^{-\beta E_i} \cdot e^{\beta F}. \tag{10.31}$$

Although we do not know the statistical expression for the free energy function F, all other variables are known from statistical considerations, thus we can express F from the above equation. To this end, let us make use of the fact that the sum of the probability density for the entire sample space (all possible states) is unit by definition, thus:

$$\sum_{\forall i} p_i = e^{\beta F} \cdot \sum_{\forall i} e^{-\beta E_i} = 1. \tag{10.32}$$

Let us introduce the following notation:

$$\sum_{\forall i} e^{-\beta E_i} = Q. \tag{10.33}$$

By inserting this into (10.32) and rearranging, we get:

$$e^{\beta F} = \frac{1}{Q}. \tag{10.34}$$

Taking the logarithm of both sides and rearranging, we obtain:

$$F = -\frac{1}{\beta} \ln Q. \tag{10.35}$$

Let us resubstitute now kT in place of $1/\beta$, and write explicitly the variables which determine Q (and also F):

$$F(T, V, N) = -kT \ln Q(T, V, N). \tag{10.36}$$

This result is the *fundamental equation* determining the function $F(T, V, N)$. Accordingly, (10.36) provides a "prescription" as to the application of the canonical ensemble in statistical thermodynamics: calculate the *canonical partition function*[7] Q as a function of the states i and the energy of these states E_i; the free energy F can be readily calculated as a function of Q.

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[7] The German name of the canonical partition function is *Zustandsumme*, literally meaning "sum of states," which has been given by Clausius. Following him, some authors still designate the canonical partition function by Z.

Comparing the relation $e^{\beta F} = 1/Q$ and (10.31), we can write the probability density of the states of the canonical ensemble in a simpler form:

$$p_i = \frac{e^{-\beta E_i}}{\sum\limits_{\forall i} e^{-\beta E_i}} = \frac{1}{Q} e^{-\beta E_i}. \tag{10.37}$$

The function F can also be written in a form similar to the microcanonical entropy. As we can read in the appendix A2.1, the Massieu function $J = -F/T$ is an entropy-like function; it is the partial Legendre-transform of the entropy function $S(U, V, N)$ with respect to the variable U. Thus, we can write from (10.36) its entropy-representation counterpart:

$$-\frac{F}{T} = k \ln Q. \tag{10.38}$$

The structure of this equation is similar to that of (10.5) specifying entropy.

Once we know the canonical probability density function, we can calculate the expectation value of the energy as well:

$$U = \sum_{\forall i} p_i E_i = \sum_{\forall i} \frac{E_i e^{-\beta E_i}}{\sum\limits_{\forall i} e^{-\beta E_i}} = \frac{\sum\limits_{\forall i} E_i e^{-\beta E_i}}{\sum\limits_{\forall i} e^{-\beta E_i}} = -\frac{\partial Q}{\partial \beta} \cdot \frac{1}{Q}. \tag{10.39}$$

In the last step, we have made use of the identity that the derivative of $e^{-\beta E_i}$ with respect to β is $E_i e^{-\beta E_i}$, and that the sum of the derivatives is equal to the derivative of the sum (which is Q). Using the chain rule to change the function to be differentiated for ln Q, we obtain that the expectation value U of the energy is simply the derivative of the function ln Q with respect to β:

$$U = -\frac{\partial \ln Q}{\partial \beta}. \tag{10.40}$$

As the notations using kT or β occur sometimes alternatively, it is also useful to change from a derivative with respect to β to the one with respect to T. Based on the chain rule and using the identity $T = 1/k\beta$, we can obtain the following relation:

$$\frac{\mathrm{d}}{\mathrm{d}\beta} = \frac{\mathrm{d}T}{\mathrm{d}\beta}\frac{\mathrm{d}}{\mathrm{d}T} = -\frac{1}{k\beta^2}\frac{\mathrm{d}}{\mathrm{d}T} = -kT^2 \frac{\mathrm{d}}{\mathrm{d}T}. \tag{10.41}$$

Applying this for the particular case of (10.40), we obtain the internal energy in the following alternative form:

$$U = kT^2 \frac{\partial \ln Q}{\partial T}. \tag{10.42}$$

Note that this can also be obtained from the expression (10.36) applying the well-known thermodynamic relation

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{V,N}. \tag{10.43}$$

10.2.1 Calculation of the Canonical Partition Function from Molecular Data

We have switched to the canonical ensemble to treat thermodynamic problems hoping that the calculation of Q will be simpler than the calculation of Ω on a microcanonical ensemble. To show this simplicity, we have to consider the following. If the states of individual molecules contained in the canonical ensemble are independent of each other, their energy is also independent, thus the energy E_i can be written as the sum of the energies of the (independent) molecular modes ε_i. The condition of this independence is that there should not be any interaction between different modes; that is, the energy of any mode should be independent of the occupancy of other modes. Using a simple and (hopefully) easy-to-follow notation, this additivity can be written as:

$$E_i = \varepsilon_1(j_1) + \varepsilon_2(j_2) + \varepsilon_3(j_3) \cdots + \varepsilon_N(j_N). \tag{10.44}$$

Here, j_1, j_2, … , j_N denote the state of individual molecules and $\varepsilon_i(j_i)$ is their energy in the element of the canonical ensemble whose energy is E_i. Putting j_i-s as subscripts, the partition function can be written as:

$$Q = \sum_{\forall i} e^{-\beta E_i} = \sum_{\forall j_k} e^{-\beta\varepsilon_{1j_1} - \beta\varepsilon_{2j_2} - \ldots - \beta\varepsilon_{Nj_N}} = \sum_{\forall j_k} \left(e^{-\beta\varepsilon_{1j_1}} \cdot e^{-\beta\varepsilon_{2j_2}} \cdot \ldots \cdot e^{-\beta\varepsilon_{Nj_N}}\right). \tag{10.45}$$

The sum of the products of exponential functions can be written as the product of the sum of exponential functions:

$$\sum_{\forall j_k} \left(e^{-\beta\varepsilon_{1j_1}} \cdot e^{-\beta\varepsilon_{2j_2}} \cdot \ldots \cdot e^{-\beta\varepsilon_{Nj_N}}\right) = \left(\sum_{j_1=1}^{M_1} e^{-\beta\varepsilon_{1j_1}}\right)\left(\sum_{j_2=1}^{M_2} e^{-\beta\varepsilon_{2j_2}}\right) \cdots \left(\sum_{j_N=1}^{M_N} e^{-\beta\varepsilon_{Nj_N}}\right). \tag{10.46}$$

The summations with respect to $j_1, j_2, \ldots, j_\mathrm{N}$ are done for the molecular states of each molecule from 1 to M_1, M_2, … , M_N; that is, for all the possible states of the molecules. (For identical molecules, these limits are obviously identical, but for a multicomponent system, they are identical for the same species only. This offers the possibility to extend statistical thermodynamics for multiple component systems.)

Let us denote the sums in parentheses by q_k and call them as the *molecular partition functions* of the species k:

$$q_k = \sum_{\forall j} e^{-\beta \varepsilon_{kj}}. \tag{10.47}$$

With the help of this molecular partition function, we can write the partition function of the canonical ensemble using (10.45) and (10.46):

$$Q = \prod_{k=1}^{N} q_k. \tag{10.48}$$

We can state that the partition function of the *ensemble* can be obtained as the product of the *molecular* partition functions calculated on the basis of the assumption of independent molecular modes.

10.2.2 Statistical Thermodynamics of the Einstein Solid and the System of Two-State Molecules in Canonical Representation

Using the previously discussed examples, we shall demonstrate the simplicity of thermodynamic calculations in the canonical representation compared to that in the microcanonical representation. Let us treat again the Einstein solid. The energy of vibrational molecular modes in this model is $n\hbar\omega_0$, with n running from 0 to infinity. As vibrations are the only possible modes, the molecular partition function can be written as:

$$q = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_0}. \tag{10.49}$$

The sum is exactly that of a geometric series with a quotient $e^{-\beta\hbar\omega_0}$:

$$q = \frac{1}{1 - e^{-\beta\hbar\omega_0}}. \tag{10.50}$$

The vibrational modes are independent of each other, thus we can calculate the total partition function of the ensemble as the product of the $3N$ identical molecular partition functions:

$$Q = \left(\frac{1}{1 - e^{-\beta\hbar\omega_0}}\right)^{3N}. \tag{10.51}$$

From this, we can readily calculate the fundamental equation providing the free energy function F:

$$F = -kT\ln Q = 3NkT\ln\left(1 - e^{-\beta\hbar\omega_0}\right) = 3nRT\ln\left(1 - e^{-\frac{\hbar\omega_0}{kT}}\right). \tag{10.52}$$

Based on the thermodynamic relation $S = -(\mathrm{d}F/\mathrm{d}T)_{V,N}$, we can also calculate the entropy function what is identical to that obtained for the extensive entropy from (10.12):

$$S = 3kN\ln\left(1 + \frac{U}{3N\hbar\omega_0}\right) + \frac{kU}{\hbar\omega_0}\ln\left(1 + \frac{3N\hbar\omega_0}{U}\right). \tag{10.53}$$

From the above discussion, it is obvious that the calculation of F is much simpler in the canonical representation than the calculation of entropy in the microcanonical representation. We can also recognize that, if there were not only one possible frequency in the crystal but more, the combinatorial calculations were rather complicated, while the canonical partition function is easy to calculate.

Let us discuss now the other previous example, the two-state system in the canonical representation. In this case, all molecules have two states whose occupancies are independent of each other. The energy of the ground state is 0, while that of the excited state is ε. Accordingly, we can write the molecular partition function as follows:

$$q = \sum_{i=1}^{2} e^{-\frac{\varepsilon_i}{kT}} = e^0 + e^{-\frac{\varepsilon}{kT}}. \tag{10.54}$$

From this, the partition function of the ensemble is easy to obtain:

$$Q = q^N = \left(1 + e^{-\frac{\varepsilon}{kT}}\right)^N. \tag{10.55}$$

The corresponding equation of state can be written as:

$$F = -kT\ln Q = -NkT\ln\left(1 + e^{-\frac{\varepsilon}{kT}}\right). \tag{10.56}$$

Using thermodynamic relations, we can get other potential functions as well. For the internal energy, we have:

$$U = -\frac{\partial\ln Q}{\partial\beta} = -N\frac{1}{1 + e^{-\beta T}}(-\varepsilon)e^{-\beta\varepsilon} = \frac{N\varepsilon e^{-\beta\varepsilon}}{(1 + e^{-\beta\varepsilon})}. \tag{10.57}$$

From this, we can deduce the entropy function according to the relation:

$$S = -\frac{F}{T} + \frac{U}{T} = -\frac{F}{T} - \frac{1}{T}\frac{\partial \ln Q}{\partial \beta}. \tag{10.58}$$

Substituting the above expression of U into (10.58), we readily get the entropy function:

$$S = Nk \ln\left(1 + e^{-\frac{\varepsilon}{kT}}\right) + \frac{N\varepsilon}{T}\frac{e^{-\frac{\varepsilon}{kT}}}{\left(1 + e^{-\frac{\varepsilon}{kT}}\right)}. \tag{10.59}$$

It is obvious also in this case that, if there were 3 (4, 5, etc.) accessible states for the molecules instead of 2, combinatorial calculations were quite involved, while the canonical partition function and hence the fundamental equation providing the function $F(T, V, N)$ is easy to calculate in these cases as well.

10.2.3 The Translational Partition Function. Statistical Thermodynamics of a Monatomic Ideal Gas

Gas molecules can have the following modes: translational modes, rotational modes, vibrational modes, and electronic modes. (We could consider in principle also *nuclear modes*, but to change their state would need enormous amounts of energy, which is not available at normal earthly conditions, thus we do not need to take them into account.)

Provided that the mentioned four modes of gas molecules are independent from each other, the partition function of the canonical ensemble can be factorized in a form $Q^{\text{trans}} \times Q^{\text{rot}} \times Q^{\text{vib}} \times Q^{\text{el}}$. Obviously, the molecular partition function can be factorized the same way: $q^{\text{trans}} \times q^{\text{rot}} \times q^{\text{vib}} \times q^{\text{el}}$, and the partition function of the ensemble can be calculated from this function. Consequently, to get the partition function, we can first calculate the molecular translational, rotational, vibrational, and electronic partition functions as its contributions.

Let us begin with the translational contribution. In an ideal gas, translational energies of the molecules are independent of each other, thus it is sufficient (in a single-component system) to consider the translational states and their energies. From quantum mechanics, we have the solution of the problem “particle in a box”. For a one-dimensional box of length L, the translational energy is

$$\varepsilon_n = \frac{n^2 h^2}{8mL^2}, \tag{10.60}$$

where the quantum number n – an integer number – runs from 1 to infinity. Let us chose the energy scale so that the lowest energy level ($n = 1$) be zero. Let us denote this energy by ε, whose value is:

$$\varepsilon = \frac{h^2}{8mL^2}. \tag{10.61}$$

As this is the zero of the energy scale, the energy depending on then translational quantum number n can be written as $\varepsilon_n = (n^2 - 1)\varepsilon$, and the molecular translational partition function as:

$$q_{1\mathrm{D}}^{\mathrm{trans}} = \sum_{n=1}^{\infty} e^{-\beta\left(n^2-1\right)\varepsilon}. \tag{10.62}$$

Translational energy levels are very much close to each other in a macroscopic system, thus we can consider the quantum number n as a continuous variable and can replace the summation by integration:

$$q_{1\mathrm{D}}^{\mathrm{trans}} = \int_1^{\infty} e^{-\beta(n^2-1)\varepsilon}\mathrm{d}n = \int_0^{\infty} e^{-\beta n^2\varepsilon}\mathrm{d}n. \tag{10.63}$$

To evaluate the integral, let us change the variable according to the substitution $x^2 = \beta n^2\varepsilon$, from which n can be explained as $n = x/\sqrt{\beta\varepsilon}$. Using the relation

$$\frac{\mathrm{d}n}{\mathrm{d}x} = \frac{1}{\sqrt{\beta\varepsilon}}, \tag{10.64}$$

we can substitute $\mathrm{d}x/\sqrt{\beta\varepsilon}$ in place of $\mathrm{d}n$, thus we can write:

$$q_{1\mathrm{D}}^{\mathrm{trans}} = \int_0^{\infty} e^{-x^2}\frac{\mathrm{d}x}{\sqrt{\beta\varepsilon}} = \sqrt{\frac{1}{\beta\varepsilon}}\cdot\frac{\sqrt{\pi}}{2} = \sqrt{\frac{\pi}{4\beta\varepsilon}}. \tag{10.65}$$

(We have substituted the value of the improper integral of the function e^{-x^2} between 0 and infinity, which is $\sqrt{\pi}/2$.) Resubstituting the expression (10.61) of ε, we get the *one-dimensional molecular translational partition function*:

$$q_{1\mathrm{D}}^{\mathrm{trans}} = \sqrt{\frac{2\pi m}{h^2\beta}}\cdot L = \sqrt{\frac{2\pi\, mkT}{h^2}}\cdot L. \tag{10.66}$$

From this expression, we can derive the three-dimensional translational partition function, knowing that the kinetic energy of the translational motion in one direction is independent from those in perpendicular directions. Thus – denoting the length of the edges of a three-dimensional box by X, Y and Z – the kinetic energies of motions in perpendicular directions add as $\varepsilon_{n_X, n_Y, n_Z} = \varepsilon_{n_X} + \varepsilon_{n_Y} + \varepsilon_{n_Z}$ and the three-dimensional translational partition function is the product of the one-dimensional partition functions; $q^{\text{trans}} = q_X \times q_Y \times q_Z$:

$$q^{\text{trans}} = \left(\frac{2\pi\, m\, k\, T}{h^2}\right)^{3/2} \cdot V, \tag{10.67}$$

where $V = XYZ$ is the volume of the box. The result is valid for a box of any shape, only the volume V matters. Let us introduce the symbol Λ for the *thermal wavelength*:

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}}. \tag{10.68}$$

Applying this notation, the molecular translational partition function can be written in the short form:

$$q^{\text{trans}} = \frac{V}{\Lambda^3}. \tag{10.69}$$

The value of the molecular translational partition function is quite large; in a gas of 100 cm^3 containing O_2 molecules at 25°C, $\Lambda = 17.8$ pm and q^{trans} has the value of 1.773×10^{30}.

In monatomic gases (e.g., noble gases), there are no other motions of molecules possible but translation. Their electronically excited states are available only at very high energies, thus we can easily calculate the fundamental equation of a monatomic ideal gas at not too high temperatures.

Following the procedure explained before to get the partition function Q, we should calculate the product of the molecular partition functions of N molecules. However, this would yield an enormously large number of which we can easily see that it is not the correct value. The previously derived calculation is namely valid only for *distinguishable* molecules – as for example in a crystal where individual molecules are localized. Gas molecules can freely move. Thus, if we interchange two molecules, it is still the same state; consequently, we do not count it as a distinct state. This suggests that the result of the products of molecular partition functions should be divided by the number of the possible interchanges of molecules that do not lead to a new state. In a gas, this is the number of permutations without repetition of N elements, that is, $N!$. Thus, the proper canonical partition function of a pure monatomic ideal gas containing N atoms is[8]:

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[8] Calculating the partition function with quantum-mechanical methods for the macroscopic states, the number of states will be correct; we do not need to include an extra division by $N!$.

$$Q = \frac{1}{N!}\left(q^{\text{trans}}\right)^N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}. \tag{10.70}$$

To calculate the fundamental equation, let us express the logarithm of the partition function applying the usual Stirling formula:

$$\ln Q = N\ln V - N\ln N + N + N\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}. \tag{10.71}$$

Rearranging and multiplying by – kT we get the fundamental equation:

$$F(T,V,N) = -NkT\left[1 + \ln\left(\frac{V}{N}\left[\frac{2\pi mkT}{h^2}\right]^{3/2}\right)\right]. \tag{10.72}$$

To obtain the equations of state, let us apply usual thermodynamic relations:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = NkT\frac{1}{V} = \frac{nRT}{V}. \tag{10.73}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = nR\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left[\frac{2\pi mkT}{h^2}\right]^{3/2}\right)\right]. \tag{10.74}$$

Differentiating the function $F(T, V, N)$ with respect to N yields the chemical potential referred to *one single particle*, thus we need to multiply it by the Avogadro constant to get the familiar molar value:

$$\mu = N_A\left(\frac{\partial F}{\partial N}\right)_{T,V} = -RT\ln\left(\left[\frac{2\pi mkT}{h^2}\right]^{3/2}\right). \tag{10.75}$$

The internal energy can be calculated using the relation $U = F + TS$, leading to the entropy-based thermal equation of state:

$$U = \frac{3}{2}nRT. \tag{10.76}$$

Inverting this function, we get the temperature T as a function of U:

$$T = \frac{2U}{3nR} = \frac{2U}{3Nk}. \tag{10.77}$$

The rationale behind this is that the wave function for the macroscopic state does not change when interchanging coordinates of gas molecules, thus it is the same state.

Inserting this in the expression (10.74) of entropy, we get the fundamental equation specifying the function $S(U, V, N)$:

$$S(U,V,N) = nR\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left[\frac{4\pi mU}{3h^2N}\right]^{3/2}\right)\right]. \tag{10.78}$$

This relation is called the *Sackur–Tetrode*[9] *equation*, commemorating the two scientists who first derived it. It is worth mentioning that the derivative of the right-hand side of (10.76) with respect to T provides the constant-volume heat capacity of the monatomic ideal gas

$$C_V = n\frac{3}{2}R, \tag{10.79}$$

which is also in accordance with experimental results.

10.2.4 Calculation of the Rotational, Vibrational, and Electronic Partition Functions

The calculation of other contributions to the partition function can be performed similarly to the method we used to calculate the translational contribution. Thus, to calculate the *rotational partition function*, we need to know the energy of molecular rotations. The energy of a linear (rigid) heteronuclear rotor – for example, an HCl molecule – can be calculated using quantum mechanics. The *rotational constant* is

$$B = \frac{h}{8\pi^2 cI}, \tag{10.80}$$

where I is the *moment of inertia* and c the velocity of light in vacuum. The energy of the rotor can be written as

$$\varepsilon^B(J) = hcBJ(J+1), \tag{10.81}$$

whence the corresponding partition function is

$$q_{\text{lin}}^R = \sum_{J=0}^{\infty}(2J+1)e^{-\beta hcBJ(J+1)}. \tag{10.82}$$

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[9] Hugo Martin Tetrode (1895–1931) Dutch theoretical physicist and Otto Sackur (1880–1914) German chemist independently derived the fundamental equation of the monatomic ideal gas and published their results in 1912. The result was named later after the two scientist. (Both died at an early age; the cause was tuberculosis for Tetrode and an unexpected explosion while developing explosives to be used in a grenade for Sackur.)

An unusual feature of this result is the factor $(2J + 1)$ appearing in the sum; we did not have anything similar in the calculations before. The reason for this factor is the following. When calculating the partition function, we sum with respect to the index J, which is the *rotational quantum number*. It is known from the quantum-mechanical description of rotation that energy levels belonging to the same rotational quantum number J have a *degeneracy* of $2J + 1$. This means that there are $2J + 1$ rotational states of energy $\varepsilon^B(J)$ at the same energy level, sharing the same quantum number J. The partition function is defined as the sum over *states*, thus all these $2J + 1$ rotational states should be added to the sum. However, as their energy is the same, we can write one exponential term having the exponent of $-\varepsilon^B(J)$, multiplied by $(2J + 1)$, the degeneracy of the energy level. (The procedure is similar in case of other degenerate levels.)

To calculate the sum, we approximate it again with an integral. This can be done if $hcB << kT$, (hcB is the energy of the ground state, $J = 0$); in this case, the values of the exponential functions with neighboring J are so close to each other that the integrand can be considered as a continuous function of J. Let us rewrite the summation as an integral, make the substitution $J(J + 1) = x$, from which $\mathrm{d}x/\mathrm{d}J = 2J + 1$, i.e., $\mathrm{d}J = \mathrm{d}x/(2J + 1)$. Thus:

$$q_{\mathrm{lin}}^R = \int_0^\infty (2J+1)e^{-\beta hcBJ(J+1)}\mathrm{d}J = \int_0^\infty (2J+1)e^{-\beta hcBx}\frac{\mathrm{d}x}{2J+1}. \qquad (10.83)$$

The integration can readily be done:

$$\int_0^\infty e^{-\beta hcBx}\mathrm{d}x = \left[-\frac{1}{\beta hcB}e^{-\beta hcBx}\right]_0^\infty = 0 + \frac{1}{\beta hcB}. \qquad (10.84)$$

Thus, the molecular partition function of the linear rotor is

$$q_{\mathrm{lin}}^R = \frac{kT}{hcB}. \qquad (10.85)$$

The heteronuclear linear rotor (e.g., the molecule HCl) has two rotational degrees of freedom. Accordingly, it has two independent rotational axes, with the same rotational constant, thus the same rotational energy.

A general rotor (e.g., a multiatomic molecule) has three rotational degrees of freedom, thus three independent rotational axes. Let us denote the corresponding rotational constants by A, B, and C. The rotational partition function of the general multiatomic molecule can then be written as:

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\sqrt{\frac{\pi}{ABC}}. \qquad (10.86)$$

The Greek letter σ denotes the *rotational symmetry factor* of the molecule. Its significance is that, when the molecule rotates through $360°/\sigma$, it results in a configuration that is indistinguishable from the one from which it started, and the same configuration occurs σ times during a complete rotation. These identical configurations cannot be considered as different states; therefore, the number of states is less, and thus the partition function should also be diminished. For the ammonia molecule, $\sigma = 3$, while for the methane molecule, it is 12, as this molecule has four threefold rotational axes. Note that, for a *homonuclear* linear rotor, two indistinguishable rotational states occur through 180° rotations. Thus, (10.85) should be modified by a division by 2 if applied for such molecules.

At ambient temperatures, many rotational excited states are occupied. Accordingly, the rotational partition function is typically of the order of magnitude of a few thousands.

The *vibrational partition function* can also be written based on the vibrational energies calculated from quantum mechanics. The energy of a harmonic oscillator can be written as

$$\varepsilon_v = \left(v + \frac{1}{2}\right)h\nu, \tag{10.87}$$

where the Latin letter v is the *vibrational quantum number*, while the Greek letter ν is the frequency of vibration. (This can be the solution of the Schrödinger equation of the molecular oscillator, or it can be determined experimentally by infrared spectroscopy.) By choosing the zero of the energy scale as

$$\varepsilon_0 = \frac{1}{2}h\nu = 0, \tag{10.88}$$

the energy of the oscillator having the quantum number v is $\varepsilon_v = vh\nu$ and the partition function

$$q^V = \sum_{v=0}^{\infty} e^{-\beta v h\nu} = \sum_{v=0}^{\infty} \left(e^{-\frac{h\nu}{kT}}\right)^v. \tag{10.89}$$

We can recognize that – similarly to (10.49) – this is a geometric series with the quotient $e^{-\frac{h\nu}{kT}}$. The sum of the series is the molecular partition function of the vibration of frequency ν:

$$q^V = \frac{1}{1 - e^{-\frac{h\nu}{kT}}}. \tag{10.90}$$

The partition function has the same form for each (harmonic) normal vibration, thus the total vibrational partition function can be written as

$$q^V = q^V(1) \cdot q^V(2) \cdot \ldots \cdot q^V(k), \tag{10.91}$$

where the k multiplicative terms comprise all the possible normal vibrational modes of the molecule. A molecule consisting of N atoms can be considered as a system of N point masses, thus it has $3N$ degrees of freedom. Of these, 3 is translational, 2 is rotational in case of a linear molecule, but it is 3 for a nonlinear multiatomic molecule. Consequently, a molecule has $3N - 5$ vibrational degrees of freedom if it is linear, and $3N - 6$ if it is nonlinear; that is, so many normal vibrational modes. Vibrational excited states have much larger energy level spacing than rotational ones, thus the value of $q^V(i)$'s at ambient temperatures is in the range 1–3.

The *electronic partition function* of molecules can also be calculated knowing the energy of the electronic ground state and the excited states. For the majority of molecules, the electronically excited state is so high that its contribution at ambient and not too much higher temperatures can be neglected to the partition function. As a result, we can assume that $q^E = 1$, except for molecules whose electronic ground state is degenerated. For these latter, the molecular electronic partition function is identical to the *electronic degeneracy*:

$$q^E = g^E. \tag{10.92}$$

An interesting exception from this rule is the case of molecules whose excited electronic states' energy is very much close to that of the ground state. For example, the NO molecule has two degenerate ground states and two degenerate excited states with only slightly higher energy. Considering its ground state energy as the zero level, its molecular electronic partition function can be written as

$$q_{\mathrm{NO}}^E = 2 + 2e^{-\frac{\varepsilon^*}{kT}}, \tag{10.93}$$

where ε^* is the energy of the excited state with respect to the ground state. (Using the same nomenclature as for the two-state system, we could call this as a "double-degenerate two-state system".)

Having calculated all the contributions to the molecular partition function in an ideal gas, we can write the partition function of the ensemble in the following form:

$$Q = \frac{1}{N!}\left(q^T \cdot q^R \cdot q^V \cdot q^E\right)^N. \tag{10.94}$$

If the ideal gas consists of K components, where there are N_j molecules of component j in the ensemble modeling the gas, the partition function can be written as:

$$Q = \prod_{j=1}^{K} \frac{1}{N_j!}\left(q_j^T \cdot q_j^R \cdot q_j^V \cdot q_j^E\right)^{N_j}. \tag{10.95}$$

This formula can be used to calculate polyatomic, multicomponent ideal gases as well. Of course, the actual form of the molecular partition function depends on the structure of molecules.

10.2.5 Statistical Characterization of the Canonical Energy

Using the canonical probability density function (10.37),

$$p_i = \frac{e^{-\frac{E_i}{kT}}}{\sum e^{-\frac{E_i}{kT}}},$$

we have calculated the expectation value of the energy (the internal energy). According to (10.40), this can be given as

$$M(E) = U = -\frac{\partial \ln Q}{\partial \beta}.$$

With the help of the probability density function, we can also calculate the variance of the internal energy. By definition, this is the expectation of the square of deviation from the expectation of the energy, and can be written as:

$$\sigma^2(E) = M\Big([E - M(E)]^2\Big) = M\Big(E^2 - 2EM(E) + [M(E)]^2\Big) = M\big(E^2\big) - [M(E)]^2. \tag{10.96}$$

Using the definition of the expectation value, we can calculate this the following way:

$$\sigma^2(E) = \sum E_i^2 \frac{e^{-\beta E_i}}{Q} - \left(\sum E_i \frac{e^{-\beta E_i}}{Q}\right)^2. \tag{10.97}$$

The second term in this equation is the square of the expectation value that we already know:

$$U^2 = \left(-\frac{\partial \ln Q}{\partial \beta}\right)^2 = \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)^2. \tag{10.98}$$

Taking into account the identity $Q = \sum e^{-\beta E_i}$, we can see that

$$\frac{\partial^2 Q}{\partial \beta^2} = \sum {E_i}^2 e^{-\beta E_i}, \tag{10.99}$$

thus we can write for the variance:

$$\sigma^2(E) = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)^2. \tag{10.100}$$

It can be seen that this is exactly the derivative of $M(E) = U$:

$$\frac{\partial M(E)}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{\partial \ln Q}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left[-\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right] = -\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} + \frac{1}{Q^2}\frac{\partial Q}{\partial \beta}\frac{\partial Q}{\partial \beta}. \quad (10.101)$$

As a conclusion, we can write the variance of energy in the following form:

$$\sigma^2(E) = -\frac{\partial M(E)}{\partial \beta} = -\frac{\partial U}{\partial \beta}. \quad (10.102)$$

By changing from the derivation with respect to β to the derivation with respect to T, as shown in (10.41), we can rewrite this as:

$$\sigma^2(E) = kT^2\left(\frac{\partial U}{\partial T}\right)_{V,N} = kT^2 N c_V. \quad (10.103)$$

The standard deviation (or *mean fluctuation*) of the energy is the square root of the above expression. Thus, we can write the *fluctuation relative to the expectation value* as:

$$\frac{\sigma}{M(E)} = \frac{\sqrt{\sigma^2}}{U} = \frac{1}{U}\sqrt{kT^2 N c_V}. \quad (10.104)$$

The extensive internal energy U in the denominator is proportional to the particle number N, thus the relative fluctuation is inversely proportional to the square root of N. With increasing N, U increases proportionally, while its relative fluctuation decreases proportionally to $1/\sqrt{N}$. As the particle number goes to infinity, the relative fluctuation of energy goes to zero. Recalling that energy is fixed in a microcanonical ensemble, we can state that in case of sufficiently large number of particles, thermodynamic properties calculated on a canonical ensemble should be the same as those calculated on a microcanonical ensemble. Let us see what is the number of particles above, of which we can neglect the canonical fluctuation of energy.

In a body of macroscopic size, the number of particles is of the order of magnitude of 10^{23}, whose square root is greater than 10^{11}. Accordingly, the fluctuation (or "uncertainty") of an internal energy of 100 kJ/mol is less than 10^{-9} kJ/mol, or 0.000000001 kJ/mol. This difference is so small that it cannot be determined using macroscopic methods; thus, the energy fluctuation can be neglected macroscopically.

We have stated that the canonical distribution over the states i is an exponential function of the energies of these states E_i:

$$p_i = \frac{e^{-\frac{E_i}{kT}}}{Q}.$$

Let us calculate from this the multiparticle energy distribution (independently of the microstate of the ensemble, the distribution of the *energy* only). The value of the microcanonical partition function $\Omega(E)$ means that the element of the canonical ensemble in which the energy is exactly E can be realized in $\Omega(E)$ different microstates. In other words, the energy level E has an $\Omega(E)$-fold degeneracy. Consequently, we should add that much (equal) probability contributions to get the probability density of energy E:

$$P(E) = \Omega(E)\frac{e^{-\beta E}}{Q} \tag{10.105}$$

The quantity $\Omega(E)$ is called the *density of states* in this respect, and it is proportional to E^N. Thus, concerning the probability of a macroscopic energy E, it contains the constant factor $1/Q$, the density of states $\Omega(E)$ (a rapidly increasing function of energy) and the Boltzmann factor $e^{-\beta E}$ (a rapidly decreasing function of energy). The probability density function of the macroscopic energy E is the product of these two functions divided by Q; it is a very sharp peak at the intersection of the rapidly increasing/decreasing functions close to their zero values. As this function emerges as a result of a large number of means of molecular energy-distributions, according to the central limit theorem, it is normally distributed, thus has the shape of a Gaussian function.

Note that while the probability density function of the multiparticle energy (i.e., the macroscopic energy of the canonical ensemble) is the sharp peak shown in Fig. 10.5, the (nondegenerate) energy levels of individual particles are distributed according to the Boltzmann distribution. In terms of the molecular energy ε_i, this can be written as:

$$p(\varepsilon_i) = \frac{1}{q}e^{-\frac{\varepsilon_i}{kT}}. \tag{10.106}$$

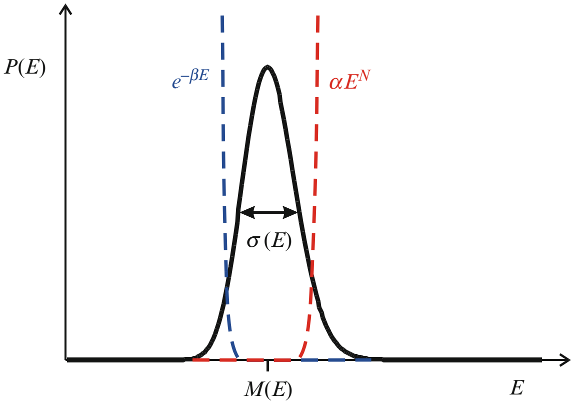


Fig. 10.5 Probability density function $P(E)$ of the multiparticle energy in a canonical ensemble

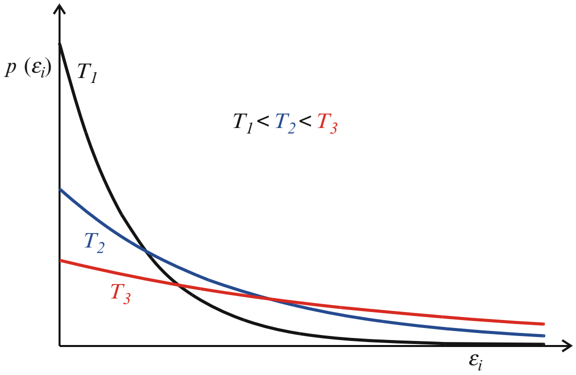


Fig. 10.6 Probability density function $p(\varepsilon_i)$ of the single-particle energy in a canonical ensemble

Figure 10.6 shows the density function of the single-particle energy at three different temperatures. As we can expect, lower-energy states are more populated at lower temperature, while increasing the temperature, higher-energy states get more and more populated. (At infinitely high temperature, the distribution would have been uniform.) The integral of the probability density function should be always unit, thus the continuous curves are lower at high temperatures close to zero energy, and higher at low temperatures. If the distribution is discrete, the sum of the possible discrete values should give unit. Thus, their height might change if the "norm" q changes, but their ratio is always the same at two different but fixed energies ε_i and ε_j:

$$\frac{p(\varepsilon_i)}{p(\varepsilon_j)} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{e^{-\frac{\varepsilon_j}{kT}}} = e^{-\frac{\varepsilon_i - \varepsilon_j}{kT}}. \tag{10.107}$$

This ratio is the same for each particle, thus the above ratio also holds for the *number* of corresponding particles:

$$\frac{N(\varepsilon_i)}{N(\varepsilon_j)} = e^{-\frac{\varepsilon_i - \varepsilon_j}{kT}}. \tag{10.108}$$

10.2.6 The Equipartition Theorem

The distribution of energy over the molecular degrees of freedom has an interesting general property. To explore this property, let us calculate the expectation value of the energy of different molecular modes in analogy of (10.40), using the single-particle energy distribution (10.106):

$$M(\varepsilon_i) = \sum \varepsilon_i p_i = -\frac{\partial \ln q}{\partial \beta}. \tag{10.109}$$

For the translational mode of 3 degrees of freedom, the molecular partition function can be written as:

$$q^T = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V. \tag{10.110}$$

By derivation with respect to β, we obtain the result:

$$-\frac{\partial \ln q^T}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\ln V + \frac{3}{2}\ln\frac{2\pi m}{h^2} - \frac{3}{2}\ln\beta\right] = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2}kT. \tag{10.111}$$

For the linear rotor of 2 rotational degrees of freedom, the molecular partition function has the form

$$q^R = \frac{kT}{hcB} = \frac{1}{\beta}\cdot\frac{1}{hcB}, \tag{10.112}$$

from which the expectation value of the energy is the following:

$$-\frac{\partial \ln q^R}{\partial \beta} = -\frac{\partial}{\partial \beta}[-\ln\beta - \ln(hcB)] = \frac{1}{\beta} = kT. \tag{10.113}$$

For the molecular vibration of 1 vibrational degree of freedom, the molecular partition function is

$$q^V = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} = \frac{1}{1 - e^{-\beta h\nu}}, \tag{10.114}$$

which leads to the expectation value of energy as follows:

$$-\frac{\partial \ln q^V}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[-\ln\left(1 - e^{-\beta h\nu}\right)\right] = \frac{1}{1 - e^{-\beta h\nu}}\cdot h\nu e^{-\beta h\nu} = \frac{h\nu}{e^{\beta h\nu} - 1} = \frac{h\nu}{e^{-\frac{h\nu}{kT}} - 1}. \tag{10.115}$$

Comparing this result to the expectation of translational and rotational energy, we can see that these latter are multiples of *kT*, while the expectation of the vibrational energy has a different form. However, if $kT >> h\nu$, the exponent in the function is much less than unit, thus we can replace the function to a good approximation by its power series, dropping higher than first-order terms. The approximation can be written as $e^{\beta h\nu} \cong 1 - \beta h\nu$, from which the expectation of the vibrational energy can be calculated in the following form:

$$\frac{h\nu}{1 + \beta h\nu - 1} = \frac{1}{\beta} = kT. \tag{10.116}$$

Table 10.2 Expectation value of the energy of different molecular modes as a function of temperature

Molecular mode	Classical mechanical expression for the energy	Expectation of energy	Expressed in terms of degrees of freedom
Translation	$\frac{1}{2}m\left(v_x^2+v_y^2+v_z^2\right)$	$\frac{3}{2}kT$	$3\cdot\frac{1}{2}kT$
Rotation	$\frac{1}{2}\left(I_1\omega_1^2+I_2\omega_2^2\right)$	$\frac{2}{2}kT$	$v^R\cdot\frac{1}{2}kT$
Vibration	$\frac{1}{2}\ \left(m\,v_x^2+kx^2\right)$	$\frac{2}{2}kT$	$2\,v^V\cdot\frac{1}{2}kT$

Thus, applying the high-temperature approximation, the expectation of the vibrational energy is also kT, provided that the vibrational energy hv is much less than kT.

Let us summarize the above results in Table 10.2, showing also classical mechanical expressions for the calculation of the energy of respective motions. Writing the expectation value of the energy as multiples of ½ kT, we can observe that it is the product of the number of degrees of freedom and ½ kT for translation and rotation, while it is twice this value for vibration.

Observing the classical mechanical expressions for the calculation of the respective energy, we can state that the energy of the translational motion of the molecule of mass m and a velocity v in the given direction is ½ mv^2. We can see a similar structure in case of the rotational energy; the momentum of inertia I replaces the mass, the angular velocity ω replaces the translational velocity, and the energy of rotation per degree of freedom is ½ $I\omega^2$. In the expression for the vibrational energy of 1 degree of freedom, there are *two quadratic terms*; ½ mv^2 describes the kinetic energy and ½ kx^2 describes the potential energy. The sum of these two terms is the total energy of vibration. In the light of these observations, we can generalize that for all (classical mechanical) quadratic terms, the expectation value of molecular energy is ½ kT, at least at high enough temperature. This is called the *equipartition theorem*.

An interesting consequence of this theorem is the expression for the heat capacity, which is the derivative of the expectation of energy with respect to temperature:

$$\frac{\partial M(E)}{\partial T}=C_V. \tag{10.117}$$

Writing this derivative for the sum of the energy terms shown in the table, relative to 1 mol, we get:

$$c_V=\frac{1}{2}R(3+v_R+2v_V). \tag{10.118}$$

According to this result, we can have information concerning the structure of the molecules from the molar heat capacity. If the molar heat capacity is 3/2 RT, the particles of the gas have only translational degrees of freedom, thus they are monatomic molecules. If $c_V = 5/2\,RT$, molecules have a linear structure, and vibrations do not play any role in the heat capacity. If c_V is greater than $5/2\,RT$, vibrational modes also contribute to the heat capacity. The greater the molar heat capacity with respect to $5/2\,RT$, the more the number of vibrational degrees of freedom can be. Prior to the development of infrared and Raman spectroscopy – which enable to identify vibrational modes of molecules, heat capacity measurements often helped to determine the structure of molecules.

10.3 General Statistical Definition and Interpretation of Entropy

Based on the expressions for the entropy on a microcanonical and a canonical ensemble, we might think that the interpretation and derivation of entropy is different on these two ensembles. However, it can be shown that entropy can be derived quite generally as a well-determined expectation value for any distribution according to the following expression:

$$S = -kM(\ln p_i) = -k\sum_{\forall i} p_i \ln p_i. \tag{10.119}$$

Obviously, entropy is the negative of the expectation of the logarithm of the probability density function multiplied by a constant. (The constant k only defines the scale of entropy.) The definition could have been written for a continuous distribution as well – by changing summation for integration – but the states in statistical thermodynamics are always discrete, in accordance with quantum mechanics, thus it is enough to deal with the formula of (10.119).

Let us first see whether the microcanonical entropy can be calculated this way, by substituting the probability density function $p_i = 1/\Omega$ into (10.119):

$$-k\sum_{i=1}^{\Omega} p_i \ln p_i = -k\sum_{i=1}^{\Omega}\frac{1}{\Omega}\ln\frac{1}{\Omega} = -k\frac{1}{\Omega}\sum_{i=1}^{\Omega} -\ln\Omega = k\frac{1}{\Omega}\cdot\Omega\ln\Omega = k\ln\Omega. \tag{10.120}$$

This result is in fact identical to the entropy calculated in (10.5).

Let us make the calculation using this time the canonical probability density function $p_i = \frac{1}{Q}e^{-\beta E_i}$:

$$-k\sum p_i\left[\ln\frac{1}{Q} - \beta E_i\right] = k\sum p_i \ln Q + k\sum p_i\beta E_i = k\ln Q + k\beta\sum\frac{E_i e^{-\beta E_i}}{Q}. \tag{10.121}$$

To calculate the result, we have made use of the fact that ln Q is not a random variable (it does not depend on the index i), thus its expectation value is itself. As to the second term, we have substituted β, which can be factored out from the summation. The first term thus yields the Massieu function $J = -F/T$, while the second term is the internal energy U (the expectation of E_i) divided by the temperature T :

$$k \ln Q + k \frac{1}{kT} \sum E_i \frac{e^{-\beta E_i}}{Q} = -\frac{F}{T} + \frac{U}{T}. \tag{10.122}$$

From the known relation $F = U - TS$, it is clear that the result is the entropy again.

We can frequently encounter the common statement that "entropy is the measure of disorder". As a matter of fact, we do not need this "explanation". We know entropy very well and can also calculate it from the postulates of (macroscopic) thermodynamics, from the results obtained in statistical thermodynamics, and in a general way, from the above definition of (10.119). Thus, entropy is a uniquely determined quantity. Let us examine, in what sense we can call it the "measure of disorder". It should be stated that – contrary to the quantitative definition of entropy – the concept "order" and "disorder" cannot be defined quantitatively, except for the regular lattice of crystals. Order and disorder in general are categories rather based on subjective judgment, thus cannot be quantified in a unique way.

Let us first consider those properties of entropy that are in accordance with the generally acceptable notion of the "measure of disorder". If the value of one of the discrete probabilities p_i in the distribution function is 1 (consequently, all the others are zero), then

$$S = -k \ln 1 = 0; \tag{10.123}$$

That is, the measure of disorder is zero if the (thermodynamic) system can only exist in one single microstate. Similarly, the mathematical theorem that the entropy is maximal for a uniform distribution is also in agreement of the intuitive concept of disorder. In this case, neither of the states is preferred, thus there is equal chance to find any of them, which is equivalent to a complete disorder. The third property supporting the analogy is that the disorder monotonously increases if the number of possibilities (states) is increased provided their distribution is uniform. Entropy always increases (being an extensive property) when the size of the system is increased. To keep the analogy, we should accept that the disorder of particles is greater if they can move in a greater space.

However, the analogy between the (nonquantitative) disorder and the (exact) entropy cannot be carried any further. To illustrate this, we shall mention a few contraindications as well. Let us examine Fig. 10.7 and tell which of the two states of the depicted containers is more ordered. Most of the spectators – if not all of them – would say that the left-hand side container – the one before mixing – is less

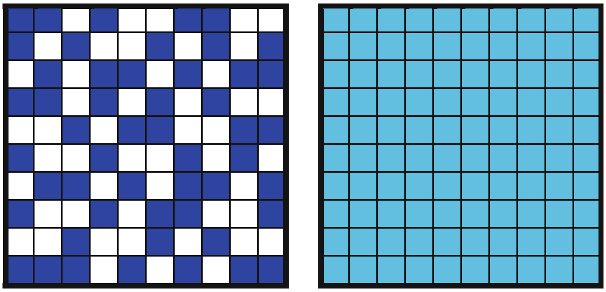


Fig. 10.7 *Left panel*: a container divided by a grid of plates into 10 × 10 compartments. Half of the compartments is chosen randomly and filled with aqueous copper sulfate solution, the other half with pure water. *Right panel*: the same container with raised grid of plates and completely mixed content

ordered than the right-hand side one. This opinion is really appropriate, as on a regular lattice, order can be measured by the regularity of occupation of positions. However, we know very well that the entropy in the right-hand container – after mixing – is greater. First, mixing is a spontaneous process, which is accompanied by an increase of entropy (in an isolated system). Second, we can readily calculate the increase of entropy by applying (6.42). Thus, we can conclude from this example that *entropy does not measure disorder*.

A similar example could be when filling in two liquids of different temperatures (say, the colder of temperature T_1 in place of the colored solutions, and the hotter of temperature T_2 in place of the water). In case of diathermal plates, the same temperature T_3 ($T_1 < T_3 < T_2$) would settle in each compartment after a while. Thus, from a more disordered initial state, a less disordered final state would be formed in a spontaneous process, while the entropy would increase. In this case, we could calculate the increase in entropy by applying (4.42).

As a third example, we can mention a supercooled liquid. Suppose we carefully cool a sample of highly purified water to –10°C without freezing, which is the initial state. After nucleation of the supercooled water with a tiny quantity of ice crystals, part of the water will freeze immediately – and spontaneously. We can state that part of the "disordered" liquid has been transformed into "ordered" crystals, thus the disorder decreased. Again, we know that this process was also spontaneous, thus the entropy increased in the isolated system – despite an increase in order. Knowing the molar heat capacities of liquid water and water ice, we can again calculate the increase of entropy. (The partial condensation of supersaturated vapor is another example.)

On the basis of the above examples, we can conclude that it is not worth considering entropy as the measure of disorder, as we can easily be mistaken taking the analogy seriously. If we want to find an analogy, the "spread" of the given distribution is a better choice. This spread is properly measured by the expression of (10.119), which is maximal if the distribution is uniform, and it decreases as we concentrate the distribution around one or several peaks.

Let us finally examine an interesting property of entropy already mentioned at the end of Sect. 2.2.1. According to Postulate 4, the entropy of any system is zero at $T = 0$ K. However, this is not always fulfilled, due to practical reasons. Quantum mechanics prescribes no degeneration at the temperature $T = 0$ K; thus, any macroscopic system should have a single possible state at this temperature. We know that at 0 K, translational and rotational motions of molecules cease to exist, their vibrational and electronic modes are in their ground state. Consequently, all contributions to the molecular partition function have the value $q = 1$, thus their product is also 1, and the Nth powers are also 1. As a result, the logarithm of Q is zero, thus the entropy is also zero.

At temperature $T = 0$ K, materials are crystalline. They also have only one single stable state at zero temperature, which also leads to zero entropy. However, this unique state at zero temperature is not always possible. If the energy of molecules at the freezing point during cooling is enough that the arrangement of the crystal can be different from that of the most stable state, this arrangement can be frozen. It means that the energy of the molecules in the crystal upon further cooling is not sufficient to change this nonequilibrium state and rearrange to a perfect crystal. Thus, the "frozen" imperfect crystal can survive for an infinitely long time and the number of possible microstates will be greater than 1 even if the temperature is arbitrarily close to zero. Accordingly, the entropy will be also greater than zero. This is called the *residual entropy*. However, such systems are *not equilibrium systems*, thus they do not question the validity of Postulate 4.

10.4 Calculation of the Chemical Equilibrium Constant from Canonical Partition Functions

To calculate the equilibrium constant, let us first express the free energy F of pure gases with the help of the total molecular partition function q:

$$F = F(0) - kT \ln Q = F(0) - kT \ln \frac{q^N}{N!}. \tag{10.124}$$

The term $F(0)$ is needed to adjust the zero level of free energy, taking into account the arbitrarily chosen zero levels when calculating contributions to the molecular partition function q.

Let us apply the Stirling formula to approximate the factorial in the above expression:

$$F = F(0) - NkT \ln q + kT(N \ln N - N) = F(0) - kT \ln q + kTN(\ln N - 1). \tag{10.125}$$

Let us substitute $R = N_A kT$ in place of NkT, thus we obtain – after some rearrangement – the following expression for the *molar* free energy:

$$F_m = F_m(0) - RT \ln \frac{q}{N_A} - RT. \tag{10.126}$$

The equilibrium constant at constant pressure and constant volume can be obtained from the reaction standard Gibbs potential $\Delta_r G^{\ominus}$; thus, we should calculate this quantity from F_m. Using the definition $G_m = F_m + PV_m$ and restricting the calculations for ideal gases, we can write PV_m in place of RT, thus obtaining the simple expression:

$$G_m = F_m(0) - RT \ln \frac{q}{N_A}. \tag{10.127}$$

As we are interested in the standard molar Gibbs potential, we have to calculate the partition function q at the standard pressure $P^{\ominus}$. Accordingly, it is the partition function in a canonical ensemble having N_A particles at temperature T, in a volume $V^{\ominus} = RT/P^{\ominus}$. Let us denote this molecular partition function by $q^{\ominus}$, and calculate the standard molar Gibbs potential as:

$$G^{\ominus} = F_m(0) - RT \ln \frac{q^{\ominus}}{N_A}. \tag{10.128}$$

We can express $F_m(0)$ based on the definition $F = U - TS$ as:

$$F_m(0) = U_m(0) - T(0)S(0). \tag{10.129}$$

By choosing $T(0) = 0$ K as the reference temperature, the term $T(0)S(0)$ vanishes, thus we can replace $F_m(0)$ by $U_m(0)$.

Now we are in a position to write the standard Gibbs potential of the general reaction $\sum_{i=1}^{r} \nu_i A_i = 0$ in the following form:

$$\Delta_r G^{\ominus} = \Delta_r U_m(0) - RT \sum_{i=1}^{r} \ln \left(\frac{q_i^{\ominus}}{N_A} \right)^{\nu_i} = \Delta_r U_m(0) - RT \ln \prod_{i=1}^{r} \left(\frac{q_i^{\ominus}}{N_A} \right)^{\nu_i}. \tag{10.130}$$

Making use of the relation $\Delta_r G^{\ominus} = -RT \ln K$, it is easy to express the equilibrium constant K. To simplify the notation, let us write $\Delta_r U_0$ in place of $\Delta_r U_m(0)$. Thus, we obtain:

$$K = \prod_{i=1}^{r} \left(\frac{q_i^{\ominus}}{N_A} \right)^{\nu_i} \cdot e^{-\frac{\Delta_r U_0}{RT}}. \tag{10.131}$$

Obviously, all we need to calculate the equilibrium constant (for ideal gas reactions) are the standard molecular partition functions of the reactive species and their zero point energies.

The above expression has a general validity if we replace the ratio $q_i^{\ominus}/N_{\mathrm{A}}$ by the molar partition function $Q_i^{\ominus}$ calculated correctly for the given species (i.e., not using the ideal gas approximation).

$$K = \prod_{i=1}^{r} \left(Q_i^{\ominus}\right)^{\nu_i} \cdot e^{-\frac{\Delta_r U_0}{RT}}. \tag{10.132}$$

The meaning of $\Delta_{\mathrm{r}} U_0$ is the same; it is the zero-point energy of the reaction. A convenient way of calculating the molar partition functions $Q_i^{\ominus}$ for interacting molecules is to derive them from molecular dynamic simulations.

Equations (10.131) and (10.132) have paramount importance in chemistry. For not too large molecules, the molecular energy can be obtained by quantum chemical methods for all molecular modes, from which the partition function can be calculated. For larger molecules, we can obtain the molecular energies from spectroscopic data. An unknown equilibrium constant can also be calculated based on the knowledge of reactants of similar chemical structure. In this case, the partition function should be decomposed into the product of nonvariable and variable factors, and the calculation of the variable factors is enough to calculate the unknown equilibrium constant. Equation (10.131) has a great importance also in reaction kinetics; transition-state theory is also based on this relation.

Due to this crucial role in chemistry, we will show the statistical thermodynamical expression of two actual reactions. The first example is a *bimolecular* reaction (with a single product)

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}, \tag{10.133}$$

whose equilibrium constant can be written as:

$$K = \frac{N_{\mathrm{A}} q_{\mathrm{C}}^{\ominus}}{q_{\mathrm{A}}^{\ominus} q_{\mathrm{B}}^{\ominus}} e^{-\frac{\Delta_r U_0}{RT}}. \tag{10.134}$$

The second one is a *unimolecular* reaction (with a single product)

$$\mathrm{A} \rightleftharpoons \mathrm{B}, \tag{10.135}$$

whose equilibrium constant can be written as:

$$K = \frac{q_{\mathrm{B}}^{\ominus}}{q_{\mathrm{A}}^{\ominus}} e^{-\frac{\Delta_r U_0}{RT}}. \tag{10.136}$$

As we can see, if the sum of the exponents in the denominator and the numerator is the same, the Avogadro constant N_{A} does not figure in the formulae.

Problems

1. Express the molar heat capacity of an Einstein solid as a function of temperature. Calculate the $T \to 0$ and $T \to \infty$ limits. Draw a plot of the molar heat capacity as a function of temperature between 0 K and 10 K (use the reference value of $u_0 = 100$ J).

Solution: Let us start from the molar entropy (10.13) of the crystal:

$$s = 3R \ln\left(1 + \frac{u}{u_0}\right) + 3R\frac{u}{u_0} \ln\left(1 + \frac{u_0}{u}\right).$$

We can calculate the temperature as

$$T = \left(\frac{\partial s}{\partial u}\right)^{-1} = \frac{u_0}{3R \ln \frac{u+u_0}{u}}.$$

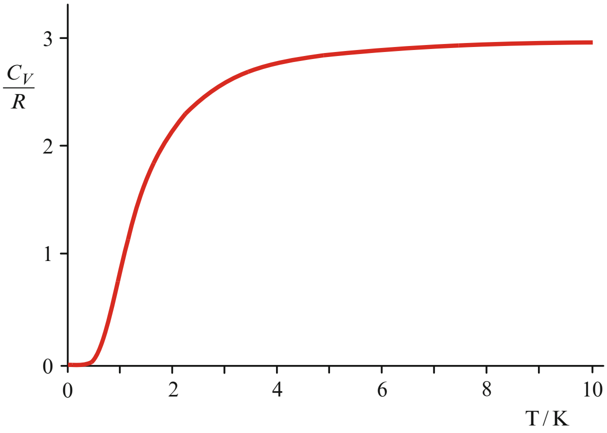
Solving the above expression for u yields the molar internal energy:

$$u = \frac{u_0}{e^{\frac{u_0}{3RT}-1}}.$$

Derivation of this function with respect to temperature directly gives the molar heat capacity:

$$c_V = \frac{\partial u}{\partial T} = \frac{u_0^2 e^{\frac{u_0}{3RT}}}{3RT^2\left(e^{\frac{u_0}{3RT}} - 1\right)}.$$

The limits are in accordance with experimental data; the $T \to 0$ limit is zero, the $T \to \infty$ limit is $3R$ (complying with the *Dulong–Petit* rule). The plot of the function from 0 to 10 K is the one below. (Note that the exponential rise is not in accordance with experimental data.)



2. Calculate the equilibrium constant of the reaction

$$\mathrm{I}_2(g) \rightleftharpoons 2\ \mathrm{I}(g)$$

at 800 K and 1 atm, supposing each component as an ideal gas, based on the following data:

$$\tilde{\nu} = 214.6\,\mathrm{cm}^{-1}; \quad B = 214.6\,\mathrm{cm}^{-1}; \quad E_\mathrm{d} = 1.5422\,\mathrm{eV}.$$

Here, $\tilde{\nu}$ is the wave number of the vibration, B is the rotational constant, and E_d is the dissociation energy (also at 0 K) of the I_2 molecule. At the given temperature, the molecule is in its nondegenerate ground state, while the iodine atom is in a degenerate electronic state having a multiplicity of 4.

Solution: We can compute the equilibrium constant K by means of the formula

$$K = \frac{\left(q_\mathrm{I}^\ominus\right)^2}{N_\mathrm{A} q_{\mathrm{I}_2}^\ominus} e^{-\frac{E_\mathrm{d}}{RT}}.$$

To compute the standard molecular partition function of the iodine atom, we only have to calculate its translational and electronic contributions, as there are no rotational or vibrational states. The electronic contribution is the number of degeneracy; $q_{\mathrm{I,el}}^\ominus = 4$. The translational contribution can be calculated using (10.67), in which m is the mass of an iodine atom:

$$m = \frac{M_\mathrm{I}}{N_\mathrm{A}} = \frac{126.90447\ \mathrm{gmol}^{-1}}{6.0220 \times 10^{23}\ \mathrm{mol}^{-1}} = 2.10734 \times 10^{-25}\ \mathrm{kg},$$

and the ideal gas molar volume V can be obtained by using the equation of state of the ideal gas:

$$V = \frac{RT}{P} = \frac{8.314\ \mathrm{Jmol}^{-1}\mathrm{K}^{-1} \cdot 800\ \mathrm{K}}{101325\ \mathrm{Pa}} = 0.06564\ \mathrm{m}^3/\mathrm{mol}.$$

Thus,

$$\begin{aligned} q_{\mathrm{I,trans}}^\ominus &= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot V \\ &= \left(\frac{2\pi \cdot 2.10734 \times 10^{-25}\ \mathrm{kg} \cdot 1.3807 \times 10^{-23}\ \mathrm{JK}^{-1} \cdot 800\ \mathrm{K}}{(6.626 \times 10^{-34}\ \mathrm{Js})^2}\right)^{3/2} \times 0.06564\mathrm{m}^3. \end{aligned}$$

The result is $q_{\mathrm{I,trans}}^\ominus = 3.992 \times 10^{32}$, which multiplied by the electronic contribution gives $q_\mathrm{I}^\ominus = 1.597 \times 10^{33}$.

To compute the standard molecular partition function of the I_2 molecule, we have to calculate all four contributions. The electronic contribution is simple, as there is only a single electronic state available; thus, $q^{\ominus}_{I_2,\mathrm{el}} = 1$. The translational contribution can be calculated similarly to the case of the iodine atom; the only difference is the molar mass, which is twice that of the atom. The result of the calculation is accordingly $2^{3/2}$ times that of $q^{\ominus}_{I,\mathrm{trans}}$; that is, $q^{\ominus}_{I_2,\mathrm{trans}} = 1.129 \times 10^{34}$. The rotational contribution can be calculated using (10.85), but with a division by 2, as the I_2 molecule is a *homonuclear* rotor, with a rotational symmetry factor of $\sigma = 2$:

$$q^{\ominus}_{I_2,\mathrm{rot}} = \frac{kT}{2hcB}.$$

When substituting the actual values, we should be careful with units. The rotational constant B is measured in cm^{-1} units, which should be multiplied by hc to yield energy. Thus, either hcB should be given in SI energy units, or kT should be given in cm^{-1} units. Choosing the latter, we can express the Boltzmann constant as $0.69503\ \mathrm{cm}^{-1}/\mathrm{K}$.[10] (As a matter of fact, a division by hc is also included.) The resulting rotational partition function is $q^{\ominus}_{I_2,\mathrm{rot}} = 7454.1$.

The vibrational contribution can be calculated using (10.90). Again, we should be careful using units. The energy of the vibration is given as the wavenumber in cm^{-1} units, thus we can use again the Boltzmann constant given above as $k = 0.69503\ \mathrm{cm}^{-1}/\mathrm{K}$ and consider the vibrational wavenumber as energy, instead of $h\nu$. The resulting vibrational partition function is $q^{\ominus}_{I_2,\mathrm{vib}} = 3.126$.

Finally, we can multiply the four contributions to get the molecular partition function $q^{\ominus}_{I_2} = 2.632 \times 10^{37}$.

When calculating the equilibrium constant, we should again take into account the units of energy. As the zero-point reaction energy is given in eV units, it is useful to use the according units of the gas constant, which is then given as $R = 5.189 \times 10^{19}\ \mathrm{eV\ K^{-1}\ mol^{-1}}$. The resulting equilibrium constant is 3.104×10^{-5}.

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[10] The reason behind the practice to use cm^{-1} as an energy unit is historical. The quantum mechanical expression for the energy of a photon is $E = h\nu$, where h is the Planck constant and ν is the frequency of the photon. The frequency can be expressed with the wavelength of the photon λ and the velocity of light in vacuum c as $\nu = c/\lambda$, while the *wavenumber* $\tilde{\nu}$ as $\tilde{\nu} = 1/\lambda$. Thus, the energy expressed as a function of the wavenumber is $E = hc\tilde{\nu}$. At the beginning of the twentieth century when quantum mechanics and spectroscopy were developing, the Planck constant was not known precisely, but wavenumbers could be measured quite precisely. This resulted in measuring optical spectroscopic energies as wavenumbers in cm^{-1} unit, which remains in use ever since. However, we should keep in mind that the energy dimension is $hc\tilde{\nu} = 1.9865 \times 10^{-23}\ \mathrm{Jcm} \times \tilde{\nu}$.

Further Reading

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