Chapter 22
The Canonical Ensemble: Notion of Distribution

Abstract The goal of statistical thermodynamics is to permit to appreciate the significance of the thermodynamic functions in terms of molecular parameters. Firstly, this chapter illustrates this point with the aid of the study of the canonical ensemble. It deals with the obtaining of the probabilities of the systems constituting the canonical ensemble to be in some energy states. It provides a description of the canonical ensemble and describes the followed strategy to calculate the average of the mechanical properties such as the pressure and energy with the help of the reasoning based on the fact that the mechanical variables have well-definite values in a given quantum state. It leads to the notion of distribution of the systems in the ensemble. It is the set of the numbers of systems found in well-defined energy states exhibiting the same composition (in one or several compounds) and the same volume. There can exist several distributions. Calculations, exemplified in the chapter, permit to obtain the elementary and global probabilities that a system of the ensemble would be in a definite energetic state. Once the probabilities are obtained, it becomes possible to calculate the canonical partition function.

Keywords Mechanical properties • Partition function • Quantum state • Supersystem • Canonical partition function • Distribution • Maximum term method • Thermodynamic function

The goal of statistical thermodynamics is to permit to appreciate the significance of the thermodynamic functions in terms of molecular parameters. Firstly, we choose to illustrate this point with the aid of the study of the canonical ensemble.

Actually, this chapter is necessary to introduce this theory. It deals with the obtaining of the probabilities of the systems constituting the canonical ensemble to be in some energy states. Obtaining these probabilities is the first necessary condition in order to be able, later, to specify the significance of some thermodynamic quantities.

The problem of the obtention of the probabilities is essentially not different from that of the determination of the distribution of the systems constituting the ensemble in the different possible energetic states. (To aim at the same goal, later, we shall consider the handling of other ensembles.)

J.-L. Burgot, *The Notion of Activity in Chemistry*,
DOI 10.1007/978-3-319-46401-5_22

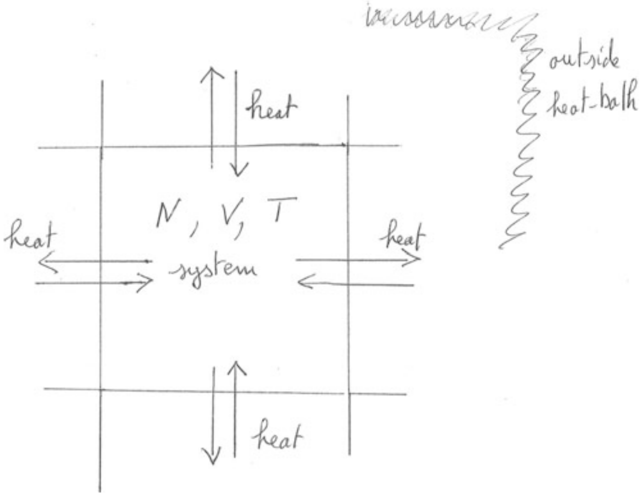

Fig. 22.1 Canonical ensemble

22.1 Description of the Canonical Ensemble (N, V, T Imposed)

The canonical ensemble is constituted by a very large number $\aleph$ ($\aleph \rightarrow \infty$) of systems replicating the thermodynamic system (under study) which, by definition, possesses the fixed volume V, the number of molecules N (there can be several types of molecules, the numbers of which N_1, N_2 … are then constant), and the temperature T uniform and constant (viz. Fig. 22.1). The partitions between the different systems are thermal conductors but do not allow the crossing of the particles through them. The ensemble is placed in a heat bath granting an equal temperature in the whole systems. The partitions of the systems are not distorting excluding, hence, no work exchange between them.

If one places an isolating membrane outside the ensemble and the whole device (ensemble + membrane) located outside the heat bath, the ensemble, now, constitutes an isolated system of volume $\aleph V$ and of number of molecules $\aleph N$ and with a total energy E_t. This isolated system is called a *supersystem*.

22.2 Strategy

Let us recall that, finally, the goal is to find the meaning of some quantities of classical thermodynamics with the help of a reasoning of statistical thermodynamics, the meaning of which being searched for in the conditions which prevail in the canonical ensemble (constant composition, temperature, volume). According to what is preceding, the problem is to calculate the average of the mechanical properties such as the pressure and the energy with the help of this reasoning. Let us notice, indeed, that since the thermodynamic system is not isolated (it is in contact with other systems of the same ensemble), its energy fluctuates.

The process entails to know the value of the quantity under study in each quantum state and to determine the number of systems of the ensemble exhibiting this quantum state. *The mechanical variables, indeed, have well-definite values in a given quantum state*. Hence, the problem is to determine the fraction of the systems of the ensemble possessing a given quantum state.

These considerations are equivalent to say that the probability P_j that a system of the ensemble is in the state of energy E_j must be known. Once known, the values of the energy $\overline{E}$ and of the pressure $\overline{p}$ can be calculated through the following expressions:

$$\overline{E} = \sum_j P_j E_j$$

$$\overline{p} = \sum_j P_j p_j$$

p_j is the pressure in the energetic state E_j; it is defined by the expression

$$p_j = -\left(\partial E_j/\partial V\right)_N$$

$-p_j\, dV = dE_j$ is the work that has to be done on the system (with a constant number of species N) in the energetic state E_j in order to increase its volume by dV. This expression is found by virtue of the quality of state function of E (viz. Appendix A). One can write, indeed,

$$dE = (\partial E/\partial V)_{N,T} dV + (\partial E/\partial T)_{N,\ V} dT$$

where by hypothesis $dT = 0$ (T imposed).

22.3 The Mathematical Problem

Let us, now, consider one system of the canonical ensemble. It is a system obeying quantum mechanics. Its characteristics depend on the values N and V which constitute the limits entailing the energy quantification (viz. quantum mechanics). As a result, there exists the collection of the following possible (authorized) energetic states written by order of increasing energy: E_1, E_2, ..., E_j. We must not forget that they are the energy states of the whole system, that is to say of a great number of particles, and not the energy states of one species. Let us recall that, for different reasons (some of which being mathematical ones), it is not possible to calculate the energy states E_j

from the Schrödinger's equation for a very large number of particles. Nevertheless, for the following reasoning, we suppose that we know them.

22.3.1 The Notion of Distribution

Since all the systems of the canonical ensemble have the same composition N (in one or several compounds) and the same volume V, everyone does possess the same quantified levels of energy E_1, E_2, …, E_{j}. (It is a consequence of the principles of quantum mechanics.) Let us suppose that we can simultaneously observe the energetic state of each system and that we are able to count the number of systems in every energetic state E_1, …, E_j. Let n_1, n_2 … be the numbers of systems found in sates E_1, E_2, …. The set of values n_1, n_2 … is a *distribution of the systems*. For each distribution, the following relations are obligatorily satisfied:

$$\sum_j n_{\mathrm{j}} = \aleph$$

$$\sum_j n_j E_j = E_t$$

where E_j is the energy of the considered system within the ensemble for the considered distribution. E_t is the energy of the ensemble (also named supersystem). (We shall see that it is not necessary to know the values $\aleph$ and E_t because they disappear during the calculations.)

Let us suppose, in order to simplify, that the ensemble possesses four systems labelized A, B, C, and D and that the possible energy states of each system are E_1, E_2, and E_3. Let us also suppose that the total energy (of the supersystem) is as follows:

$$E_t = E_1 + 2E_2 + E_3 \tag{22.1}$$

that is to say $n_1 = 1$, $n_2 = 2$, and $n_3 = 1$. These values (E_t, E_1, E_2, E_3, n_1, n_2, n_3) define the distribution.

22.3.2 The Notion of Sub-distribution

There are several possibilities of attribution of the energies E_1, E_2, and E_3 to the systems A, B, C, and D in order that the distribution defined by relation (22.1) exists. They are those mentioned in Table 22.1. We call them "sub-distributions" (personal terminology).

We notice that there are 12 sub-distributions corresponding to the same distribution, labelized k. This result is no more than the solution of the classical problem

Table 22.1 Sub-distributions corresponding to the distribution $n_1 = 1$, $n_2 = 2$, and $n_3 = 1$; $N = 4$, labelized systems A, B, C, and D

A	B	C	D
E_2	E_2	E_3	E_1
E_2	E_3	E_2	E_1
E_3	E_2	E_2	E_1
E_2	E_2	E_1	E_3
E_2	E_3	E_1	E_2
E_3	E_2	E_1	E_2
E_3	E_1	E_2	E_2
E_2	E_1	E_3	E_2
E_2	E_1	E_2	E_3
E_1	E_3	E_2	E_2
E_1	E_2	E_3	E_2
E_1	E_2	E_2	E_3

of combinatory analysis which, in this case, can be presented by giving the answer to the following question: How many (number Ω) possibilities to group 4 objects by groups of 2, 1, and 1 do exist? The answer is

$$\Omega = (2 + 1 + 1)!/(2\,!1\,!1\,!) = 12$$

From the general viewpoint, the number Ω of possibilities to group $(n_1 + n_2 + \ldots n_j)$ objects by groups of n_1, n_2, …, n_j objects is given by the relation

$$\Omega = \left(n_1 + n_2 + \ldots n_j\right)\,!\,/\,\left(n_1\,!\,n_2\,!\ldots n_j\,!\right) \tag{22.2}$$

Let us recall that all the sub-distributions have the same energy.

22.3.3 Case of Several Distributions

We must bear in mind that there are numerous distributions existing for the same set of parameters N, V, and T. For the same example as previously, let us suppose that it is the case for the distribution $n_1 = 2$, $n_2 = 0$, and $n_3 = 2$, that is to say

$$2E_1 + 0E_2 + 2E_3 = E_t$$

where the energy E_t is the same as that of the preceding distribution. This new distribution exists under $(2 + 0 + 2)\,!/(2\,!0\,!2\,!) = 6$ sub-distributions. Let us also suppose that only two distributions exist for the same total energy. Since they possess the same energy E_t, according to the second postulate, the sub-distributions of both distributions are equiprobable, whichever their origin.

What is being searched for is the probability to find a system of the ensemble in the energy state E_j, that is to say, remaining in the same example as previously, the

Table 22.2 Sub-distributions of the same total energy *E* and, hence, of the same probability stemming from two distributions (see text)

A	B	C	D
E_2	E_2	E_3	E_1
E_2	E_3	E_2	E_1
E_3	E_2	E_2	E_1
E_2	E_2	E_1	E_3
E_2	E_3	E_1	E_2
E_3	E_2	E_1	E_2 (1$^{\text{ère}}$ distribution)
E_3	E_1	E_2	E_2
E_2	E_1	E_3	E_2
E_2	E_1	E_2	E_3
E_1	E_3	E_2	E_2
E_1	E_2	E_3	E_2
E_1	E_2	E_2	E_2
E_1	E_1	E_3	E_3
E_1	E_3	E_1	E_3
E_3	E_1	E_3	E_1
E_3	E_1	E_1	E_3 (2$^{\text{ème}}$ distribution)
E_3	E_3	E_1	E_1
E_1	E_3	E_3	E_1

probability to find the system *A* or *B* or *C* or *D* with the energy E_1, E_2, or E_3. In this very simple example, the result can be found by a direct numbering by placing in the same table all the sub-distributions and by performing the numbering.

The direct numbering indicates that each system *A*, *B*, *C*, or *D* possesses 1/3 chance to possess the quantified energy levels E_1, E_2, and E_3. (The fact that all these probabilities are all equal (1/3) must not be generalized. It results solely from the chosen numerical values. It must be considered as a numerical accident (Table 22.2).)

The direct numbering is not, of course, envisageable in statistical thermodynamics, given the huge number of the existing distributions and sub-distributions. Fortunately, there exists a useful mathematical relation which generalizes what is preceding. It results from the following reasoning:

- The elementary probability prob_1 (1 because it concerns the first distribution) in order that one of the systems *A*, *B*, *C*, or *D* possesses the energy E_2 in the first distribution is 2/4 since $n_2 = 2$ and since there are four systems. The number of times that one of the systems in the first distribution is endowed with the energy E_2 is $12 \times 2/4 = 6$, that is to say by generalizing $\Omega_1 \bullet \text{prob}_1$.
- The elementary probability prob_2 in order that one of the systems possesses the energy E_2 in the distribution 2 is $6 \times 0/4 = 0$, that is to say $\Omega_2 \bullet \text{prob}_2$.
- The total number of possibilities that a system would be in an ordinary state of energy is this example $12 + 6 = 18$, that is, $\Omega_1 + \Omega_2$. The global probability (and not elementary) P_2 that a system would be in the energetic state E_2 is as follows:

$$P_2 = (12 \times 2/4 + 6 \times 0/4)\ /\ (12 + 6) = 1/\ 3$$

and by generalizing

$$P_j = \left(\sum_j \text{prob}_j \Omega_k\right) \Big/ \sum_k \Omega_k \tag{22.3}$$

where j marks the authorized state of energy of the system. prob_j is the elementary probability in order that in the distribution k, the energy be E_j.

- The probability P_2 can also be written (in a strictly equivalent manner) as

$$P_2 = (1/4)(2 \times 12 + 0 \times 6)/(12 + 6)$$

where 4 is the number of systems and 2×12 and 0×6 are the numbers of times that the state of energy E_2, respectively, appears in the first and second distribution.

The general relation (22.3) can also be written according to

$$P_j = (1/\aleph) \left(\sum_k n_j \Omega_k\right) \Big/ \sum_k \Omega_k \tag{22.4}$$

This expression is a generalization of the preceding which gave P_2.

22.4 Obtention of P_j

22.4.1 Great Number of Distributions: Method of the Maximal Term

The obtaining of P_j is performed in a mathematical way. It is based on the fact that there exist numerous possible distributions obeying the constraints of the problem. The latter ones are

- The number $\aleph$ of systems of the ensemble
- The temperature T
- The different possible energies E_j of every system. (They depend on the total number of particles N and of the volume V, according to the principles of quantum mechanics.)

Given the very large number $\aleph$, one demonstrates that one distribution weighs much more and even quasi-infinitely more than other ones. Therefore, one can make the assumption that it entails its repartition of the systems in the ensemble, and it is done as a function of the energies E_j. The hypothesis is entitled "method of the maximal term." From the mathematical standpoint, it consists in replacing the logarithm of a sum by the logarithm of the highest term of the sum, when the latter is constituted of very numerous terms. The expression giving the probability P_j to find a system of the ensemble in the energetic state E_j is constituted of very numerous terms. Taking only into account the largest term seems to be an approximation. It is the case, but it does not lead to any detectable error. (viz. Appendix A).

By applying the hypothesis, the relation (22.4) reduces to

$$P_j = n_j^* / \aleph$$

where n_j^* is the number of times that the quanto-energetic state E_j appears in the most probable distribution. Of course, there are as many n_j^* to calculate as quanto-energetic E_j levels do exist.

Hence, the most probable distribution must be found.

22.4.2 Calculations

The calculations are performed by starting from ln Ω rather than from Ω. It is easier to process in such a manner and it does not change anything concerning the result since ln x varies as x.

According to the expression (22.2), we obtain

$$\ln \Omega = \ln\left[\left(n_1 + n_2 + \ldots n_j\right)!\right] - \ln n_1\,! - \ln n_2\,! - \ \ldots \ln n_{\mathrm{j}}!$$

Then, they are performed by using Stirling's approximation which is written as

$$\ln y\,! \approx y \ln y - y$$

The use of this approximation is all the more justified as y is a large number. This is the case here. With this approximation, ln Ω becomes

$$\begin{aligned} \ln \Omega = & \left(n_1 + n_2 + \ldots\ n_j\right) \ln\left(n_1 + n_2 + \ldots\ n_j\right) - \left(n_1 + n_2 + \ldots\ n_j\right) - n_1 \ln n_1 \\ & + n_1 - n_2 \ln n_2 + n_2 \ldots\ldots - n_j \ln n_j + n_j \end{aligned}$$

The mathematical process coming immediately in mind is to have to successively vanish the partial derivatives (∂ ln Ω/∂n_1), (∂ ln Ω/∂n_2) … (∂ ln Ω/∂n_j) and, from this process, to extract the values n_1, n_2, …, n_j leading to this result. But, there is a difficulty: the mathematical system is submitted to the following constraints:

$$\begin{aligned} & n_1 + n_2 + \ \ldots n_j = \aleph \\ & n_1E_1 + n_2E_2 + \ \ldots n_jE_j = E_t \end{aligned}$$

The smartest means permitting this process of maximalization taking into account these constraints is to use the method of Lagrange's multipliers (viz. Appendix A) which, in this case, translates itself into the successive vanishing of the partial derivatives with respect to n_1, n_2, …, n_j of function F, and no longer of function ln Ω:

$$F = \ln\Omega - \alpha\left(n_1 + n_2 + \ldots n_j\right) - \beta\left(n_1E_1 + n_2E_2 + \ldots n_jE_j\right)$$

where α and β are two constants, the physical meaning of which will appear in the following calculations.

When the calculation of the derivatives is performed, we obtain the following relations:

$$\begin{aligned} n_1 &= \aleph\ \mathrm{e}^{-\alpha-\beta E_1} \\ n_2 &= \aleph\ \mathrm{e}^{-\alpha-\beta E_2} \\ n_j &= \aleph\ \mathrm{e}^{-\alpha-\beta E_j} \end{aligned} \tag{22.5}$$

These relations are very important. We can deduce the following points from them:

- The signification of the constant e^{α}.

  Since $\Sigma_{\mathrm{j}}\ n_j = \aleph$, the addition of relations (22.5) leads to

  $$\mathrm{e}^{\alpha} = \mathrm{e}^{-\beta E_1} + \mathrm{e}^{-\beta E_2} + \ldots \mathrm{e}^{-\beta E_j}$$

- The mean energy $\overline{E}$ of each system.

  Since $E_t = \aleph\ \overline{E}$,

  $$\sum_j n_jE_j = \aleph\overline{E}$$

By replacing the n_j by their expressions (22.5) and $\mathrm{e}^{-\alpha}$ by the above expression, we obtain

$$\overline{E} = \sum_j E_j\mathrm{e}^{-\beta E_j} / \sum_j \mathrm{e}^{-\beta E_j} \tag{22.6}$$

It is important to notice that, according to the expression (22.6), the parameter β appears as being an implicit function of the mean energy $\overline{E}$ and also, therefore, of the composition N and of the volume V which govern the quantum levels E_j. It is the same for α which depends on the same parameters. But, actually, the studied ensemble is that defined by the macroscopic parameters N, V, and T and not by N, V, and $\overline{E}$. However, as we shall see, $\overline{E}$ depends on T. Let us anticipate what is following by mentioning that β is inversely proportional to the absolute temperature. More precisely, $\beta = 1/kT$ where k is Boltzmann's constant and T the absolute temperature.

- The expression giving the probability P_j to find a system of the ensemble in the energetic state E_j is constituted of very numerous terms. Taking only into account the largest term seems to be an approximation. It is the case, but it does not lead to any detectable error.

It is calculated by applying the general definition of a probability, through the relation

$$P_j = n_j/\aleph$$

By replacing n_j by its expression (22.5) and by introducing the above expression $e^{-\alpha}$, we find

$$P_j = e^{-\beta E_j}/\sum_i e^{-\beta E_i} \tag{22.7}$$

We shall see in the following chapter that these expressions permit to grasp the meaning at the molecular scale of the great thermodynamic functions.

The expressions (22.6) and (22.7) call for the great importance of the sum $\Sigma_i e^{-\beta E_i}$. Indeed, it will play a considerable part. In statistical thermodynamics, such a function is called *partition function*. As it happens here, it is the partition function of the canonical ensemble. It is symbolized by Q:

$$Q = \sum_i e^{-\beta E_i}$$