

## Chapter 25

# Systems of Molecules or Subsystems: Independent, Distinguishable, and “Indistinguishable”

**Abstract** In this chapter are given some general principles permitting the study of systems composed of atoms, molecules, groups of molecules, and independent “subsystems,” with the aid of statistical thermodynamics. “Subsystems” are defined as, for example, the different degrees of freedom in the same molecule (such as translational, rotational a.s.f.). They can also be the molecules adsorbed on independent adsorption sites located on a solid surface . . . a.s.f.

The meaning of independent being specified, the cases of the molecules or “subsystems” distinguishable and “indistinguishable” are studied. The invoked calculations in this chapter are based on the handling of the canonical partition function. Such calculations induce the introduction of a new kind of a partition function, the molecular partition one.

**Keywords** Adsorption sites • Subsystems • Distinguishable and indistinguishable systems and subsystems • Degrees of freedom • Maxwell–Boltzmann statistics • Molecular partition function • Translational, rotational quanta-energetic states

In this chapter, we recall some general principles permitting the study of systems composed of atoms, molecules, groups of molecules, and independent “subsystems,” with the aid of statistical thermodynamics. For example, we call “subsystem” the different degrees of freedom in the same molecule (such as translational, rotational, a.s.f.). It can also be the molecules adsorbed on independent adsorption sites located on a solid surface . . . a.s.f.

After having specified what we mean by independent, we successively envisage the cases of the molecules or “subsystems” distinguishable and “indistinguishable.” This chapter is based, in the different cases, on the structure of the partition function.

## 25.1 Meaning of the Independence of the Molecules and “Subsystems”

One can consider that the particles, present in the same container, are independent from each other when their displacement is not influenced by that of another. Each particle exhibits a purely random displacement in the container. The lack of

independence of atoms, molecules constituting the system, may be due to physical interactions between the components or to some restrictions of symmetry regarding the wave functions describing the system. The latter case is not envisaged here.

Actually, the strict independence of the components of the system cannot enter within the framework of this study, since in such a case, the studied system cannot reach the internal state of equilibrium. The statistical study of such systems becomes, then, very difficult, if not impossible. Let us specify this point by, for example, briefly, considering the case of perfect gases. Their density in the container must be sufficiently weak so that the intermolecular forces do not play a part in the properties of the gases. However, the internal equilibrium (entailing that the perfect gas law is satisfied) must be still reached by the collisions between the molecules out by the collisions between the latter with the partitions of the container in order that the thermodynamic properties of such systems do exist.

## 25.2 Calculation of the Partition Function of Independent and Distinguishable Molecules or Subsystems

Since the thermodynamic properties of a system may be obtained from its partition function, the latter must be calculated.

### 25.2.1 *Definition of the System*

Let us regard the case of one container of volume  $V$ , only containing two molecules of different natures. Let  $\varepsilon_0, \varepsilon_1, \varepsilon_2$ , and so forth be the quantified energies of the first molecule, and  $\varepsilon'_0, \varepsilon'_1, \varepsilon'_2$  and so forth those of the second molecule. (These possible energies are obtained by resolution of the Schrödinger's equation related to each kind of molecule.)

- The independence of the particles is expressed by the fact that, since by hypothesis both molecules do not exhibit noticeable interactions between them, the energy of the system constituted by both kinds of molecules in the volume  $V$  is the sum of the energies of the individual molecules, which are those they possess when they are alone in the volume  $V$ .
- Clearly, in the previous reasoning, the particles are distinguishable. That is shown by the fact that the possible energies  $\varepsilon_i, \varepsilon'_i$  are distinctly marked.

### 25.2.2 Calculation of the Partition Function

In the above example, it is evident that, since the molecules are independent, when one is in the state of energy  $\varepsilon_i$ , the other may be found in every authorized other one  $\varepsilon'_j$ . As a result, the partition function  $Q$  of the whole system is given by the expression

$$Q = e^{-(\varepsilon_0+\varepsilon'_0)/kT} + e^{-(\varepsilon_0+\varepsilon'_1)/kT} + e^{-(\varepsilon_0+\varepsilon'_2)/kT} \\ + e^{-(\varepsilon_1+\varepsilon'_0)/kT} + e^{-(\varepsilon_1+\varepsilon'_1)/kT} + e^{-(\varepsilon_1+\varepsilon'_2)/kT} \\ + e^{-(\varepsilon_2+\varepsilon'_0)/kT} + \text{asf} \dots$$

That is,

$$Q = \sum_i e^{-\varepsilon_i/kT} \left( \sum_j e^{-\varepsilon'_j/kT} \right)$$

When the energy states  $\varepsilon_i$  are degenerated  $\omega_i$  times and those  $\varepsilon'_j/\omega'_j$  times, the partition function  $Q$  is given by the relation (viz. Chap. 22)

$$Q = \left( \sum_i \omega_i e^{-\varepsilon_i/kT} \right) \left( \sum_j \omega'_j e^{-\varepsilon'_j/kT} \right)$$

The functions  $\left( \sum_i e^{-\varepsilon_i/kT}, \sum_j e^{-\varepsilon'_j/kT} \right)$ ,  $\sum_i \omega_i e^{-\varepsilon_i/kT}$ , and  $\sum_j \omega'_j e^{-\varepsilon'_j/kT}$  are called molecular partition functions. They must not be confused with the partition function of the whole system  $Q$ . The former are symbolized by  $q$ .

Generalizing the foregoing example, we can deduce that in the case of systems constituted by molecules or subsystems independent and distinguishable, the partition function of the system  $Q$  is given by the relation

$$Q = q_1 q_2 q_3 \dots \quad (\text{independent and distinguishable particles}) \quad (25.1)$$

where  $q_1, q_2, q_3 \dots$  are the molecular partition functions of the molecules 1, 2, 3 ... or of the subsystems 1, 2, 3, and so forth.

### 25.3 Independent and “Indistinguishable” Molecules or Subsystems

It is the case for example in which the molecules are identical and, hence, “indistinguishable,” while not being in interactions by hypothesis, i.e., still independent from each other.

The calculation of the partition function stems from the following reasoning. Relation (1), if it was legitimate, would be in this case

$$Q = q^N$$

where the molecular partition function  $q$  is the same for each molecule (or each subsystem) since the molecules are identical and are contained in the same volume  $V$ .

Actually, this relation is not exact. So, we adopt the same reasoning as in the example above concerning both kinds of molecules; it appears, for example, that the state energy of the previous system  $\varepsilon_0 + \varepsilon_1'$  of the foregoing example is, now, equal to the energy of the state  $\varepsilon_0' + \varepsilon_1$  of the former example, since in this new case  $\varepsilon_1' = \varepsilon_1$ . It is the same thing for all the states where  $i \neq j$ . As a result, in this case where there are two molecules, these “crossed” terms appear two times with the preceding numeration system. It is clear that they must be counted only once in the calculation of the partition function of the system. The generalization of this result leads to the fact that for a system constituted by  $N$  identical molecules, the crossed terms would appear  $N!$  times. The adopted solution in order to calculate  $Q$  is to use the relation

$$Q = q^N / N! \quad (\text{independent and “indistinguishable” particles}) \quad (25.2)$$

However, by calculating in such a way, we are making an error since we also divide the “non-crossed” terms of energy  $\varepsilon_i + \varepsilon_i$  by  $N!$  the “non-crossed” terms of energy  $\varepsilon_i + \varepsilon_i$  which do appear only once during the preceding numeration. But, this error may be qualified justifiably as being perfectly negligible since, given the number of molecules  $N$  excessively large (of the order of  $10^{20}$ ), the number of “crossed terms” is incomparably larger than that of the “non-crossed” ones and as a result the latter ones are negligible in the sum  $Q$ .

*Let us mention the important following point :the relation (25.2) is legitimate if only the number of quanta-energetic states is by far larger than the number  $N$ . In these conditions, it proves to be correct that all the terms bringing an important contribution to the partition function  $Q$  correspond to the fact that each molecule is in a different quanta-energetic state. It is said, then, that the kind of statistics which is obeyed is that of Maxwell–Boltzmann.*